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TOXAPHENE APPLICATION AND FISH STOCKING IN ALBERTA LAKES: EFFECTS ON BIOTA, AND TOXAPHENE RESIDUES IN FISH AND SEDIMENTS 30 YEARS LATER

by

BRENDA MARGARET MISKIMMIN

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY.

IN

DEPARTMENT OF BIOLOGICAL SCIENCES

EDMONTON, ALBERTA

SPRING 1995

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled "Toxaphene application and fish stocking in Alberta lakes: effects on invertebrates and toxaphene residues in fish and sediments 30 years later", submitted by **Brenda Margaret Miskimmin** in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY.

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DATE: 13 December 1994

ABSTRACT

I hypothesized that the fishery management practices of toxaphene application and trout stocking would affect non-target organisms in lakes. Because these practices were rarely monitored in the past, I analysed cladoceran, dipteran and algal pigment fossils in sediment cores from Peanut (treated and untreated basins), Chatwin and Annette Lakes treated 30+ years ago to determine the long-term response of organisms near the base of the food chain. I also examined residual toxaphene concentrations in sediment cores from all four basins and in stocked fish from Peanut and Chatwin Lakes.

In the lake that received the highest toxaphene concentration (Chatwin), planktonic cladocerans decreased in abundance, and dominance quickly changed from small to large-bodied types. *Bosmina* was reduced by 88% at the time of toxaphene application, and was eliminated during the 1970's as invertebrate predators like *Chaoborus americanus* increased in response to the poor survival of stocked fish. Chydorids were remarkably resistant to both poisoning and fish stocking. The lakes appear to have had enhanced algal pigment preservation following treatment, as deduced by fossil pigment deposition. Also, the oligotrophic lake (Annette) underwent significant compositional changes in its algal assemblage coincident with toxaphene treatment. Toxicity to total chironomids was not detected in any of the lakes, although genera-specific responses were not analysed.

Toxaphene remained elevated in sediments from these lakes 30 to 35 years after treatment. Analysis of chlorobornanes (CHBs) using gas chromatography/mass spectrometry showed that sediments deposited at the time of treatment contained high concentrations of hepta-, octa-, and nonachlorobornanes with a similar gas chromatographic peak pattern to technical toxaphene. In contrast, the near-surface sediments contained a dominant heptachlorobornane, in proportions not normally observed in environmental samples, or in the technical product. Analyses of fish revealed a toxaphene "fingerprint" similar to that of the degraded material in sediments, suggesting that the chemical was both water soluble and bioavailable.

Toxaphene application clearly caused more than short-term problems in these ecosystems. The manipulation of fish communities was primarily responsible for long-term changes in the invertebrates of all three lakes. Significant residual CHBs in surface sediments and in fish today suggest that other toxaphene-treated lakes should be re-examined.

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Robert Flett (Flett Research) helped date my cores with ^{210}Pb analyses, and Malcolm Stephenson (AECL) provided additional ^{210}Pb and ^{137}Cs analyses. Alberta Fish & Wildlife allowed free access to their historical records; Mike Sullivan and Hugh Norris provided rainbow trout from Peanut and Chatwin Lakes. E.E. Prepas provided archived plankton samples from Peanut Lake. Janis Cook and C. Lee Van On were excellent summer field and laboratory assistants. I am truly appreciative of their hundreds of painstaking hours spent at the microscope. Brian Parker was helpful in the field, on the computer, and answering any fishy or other questions I had.

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I owe thanks to Peter Leavitt for introducing me to plant pigments as useful paleolimnological indicators. He and Alistair Hardie guided me through the intricate steps of sampling, HPLC analysis and identification of sedimentary pigments.

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I. GENERAL INTRODUCTION

In the late 1950's and early 1960's, toxaphene became popular as a piscicide due to its high toxicity to fish. It was a cheaper and more lethal alternative to the most commonly used piscicide, rotenone (Cumming 1973). Toxaphene was applied to at least nine Alberta lakes to extirpate native fish in preparation for trout stocking. Once fishery managers realized that stocked trout in some lakes failed to survive for many years because of residual toxaphene, its use was gradually curtailed.

The extent of the toxicity to non-target organisms and the persistence of toxaphene was not appreciated until years after numerous North American lakes had been treated. It was too late by that time to establish the natural variability of communities prior to the perturbation. A few reported that toxaphene had extirpated invertebrates in lakes in addition to fish (Webb 1980; Larkin et al. 1970; Hilsenhoff 1971). All of these researchers sampled one treated lake only once prior to treatment, and a few times after treatment. With one exception, effects on only benthic macroinvertebrates for a maximum of 4 years following treatment were reported (Webb 1980; Hilsenhoff 1971). Larkin et al. (1970) completed a similar study of Paul Lake B.C., that included treatment effects on both benthic invertebrates and zooplankton. No one attempted to examine the response of the littoral microcrustaceans, the Chydoridae. Further, when stocked fish that survived in treated lakes were examined within 1-3 years after treatment, they were found to contain elevated concentrations of toxaphene (Terriere et al. 1966; Hughes and Lee 1973). No toxaphene-treated lakes were evaluated to determine whether toxaphene remained in the ecosystems many years after the original application.

Replacing native fish with stocked trout can further alter the composition of invertebrate communities because of differences in the feeding habits of native species and hatchery fish. For example, when piscivores are added to lakes, zooplankton biomass and body size increases because of selective predation on planktivorous fish (Carpenter et al. 1987). When planktivory is reduced, large invertebrate predators increase and in turn, their small-bodied prey are strongly regulated (Elser et al. 1987). The degree of resilience of ecological communities in the face of multiple perturbations that extend for decades (or more) can only be understood by either long-term monitoring or paleoecological studies.

My thesis examines 3 toxaphene-treated and 1 untreated lake in Alberta (see Maps; Alberta, Fig. I-1; Canada, Appendix A) and extends the above studies that surveyed the effects of toxaphene on non-target organisms. It further combines these results with the long-term effect of trout stocking. Using paleolimnological techniques, I was able to establish at least two decades of natural variability within the lakes prior to the perturbations. My original objective was to examine the effect of toxaphene and trout stocking on non-target organisms in Peanut (Treated), Chatwin and Annette Lakes, treated between 1957 and 1962. In the course of these studies, it became evident that toxaphene had not become "buried" and is still a contaminant the treated lakes today. This expanded the scope of my study from a paleolimnological examination of historical effects on plants and invertebrates, to quantification of residual toxaphene in contemporary sediments and fish.

Figure I-1: Map of Alberta indicating lakes that are known to have been treated with toxaphene. Underlined lakes were examined during this thesis research. Map modified from Times Atlas of the World, 9th Ed., Random House (1992).

Chapter II reconstructs a 50-year record of the effect of toxaphene and trout stocking on planktonic Cladocera, *Chaoborus* spp. and Chironomidae in Peanut Lake and Chatwin Lake, Alberta. Because Peanut Lake was divided into two basins by berm construction prior to treating only one side with toxaphene, I cored the untreated basin to compare with results from the treated lakes. Chapter III compares the effects on littoral Cladocera (Chydoridae) between the oligotrophic montane Annette Lake, and the hypereutrophic Chatwin Lake. Chapter IV examines toxaphene residues in sediments and fish, highlighting the mobility and bioaccumulation of important degradation products that dominate samples from treated lakes. Chapter II was published in *Canadian Journal of Fisheries & Aquatic Sciences*, and Chapters III and IV are in review with *Freshwater Biology* and *Environmental Science & Technology*, respectively.

The following is an introduction to the techniques, materials, and organisms utilized during the course of my research.

Paleolimnology as a long-term monitoring tool

The best understanding of ecosystems comes from long-term data sets that allow background conditions to be assessed (reference conditions), natural variability to be established, and likely future scenarios to be inferred (Smol 1992). Further, assessment of the effects of perturbation requires before and after data that are rarely available. Paleolimnology offers substitute methodologies that reconstruct background conditions and establish a long-term chronology of unrecorded events in and around lakes.

Paleolimnological techniques and monitoring techniques are complementary and overlap in timescales (Fig. I-2; Smol 1992 p.51). Historical monitoring rarely is done in the order of decades, whereas paleolimnological assessments can cover hundreds, sometimes thousands of years. On the other hand, not all organisms within all groups that reside in lakes are preserved in sediments (eg. copepods, amphipods), a fact that limits most paleolimnological inferences. Unfortunately, reconstructions are further constrained by a lack of knowledge of the contemporary ecology of the organisms in question (eg. Chydoridae and Chironomidae). Witnin acknowledged limitations, and using other available historical data, paleolimnological reconstructions are extremely useful in

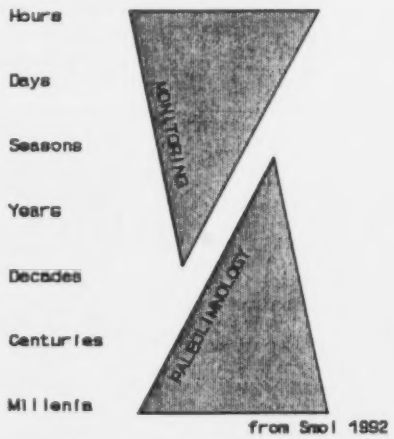


Figure I-2: Relative time scales of environmental monitoring and paleolimnology (from Smol 1992).

replacing missing records.

The range of analyses that have been employed in paleolimnology is extensive, inferring climate change (Reasoner and Hickman 1989; Hickman et al. 1990; Hickman and Schweger 1993), lake acidification (Charles and Smol 1988; Davis et al. 1985 and 1990), forest fires (Hickman et al. 1990), food web changes (Leavitt et al. 1989), various pollution problems (Warwick 1989; Stansfield et al. 1989), changes in trophic status (Hickman and Schweger 1991), and others (Table I-1).

Sediments

Surface sediments accumulate by the constant accrual of organic and inorganic matter from dead invertebrates, fecal pellets, minerals, remains of algae and other plant material, leaves, and pollen (Table I-1). Labile components of this material are decomposed or metabolized by detritus feeders, bacteria and fungi, leaving more resistant materials such as chitin, lignin, diatom frustules, pollen grains, resistant pigments, cellulose and other organic and inorganic materials (Frey 1969). Remains of many organisms living outside and within the lake become integrated and "focused" (Lehman 1975) in the deepest profundal sites. The invertebrate remains that are discussed in this thesis originate from the planktonic, benthic or littoral communities of lakes. Headshields, carapaces, claws and/or mandibles composed of refractory chitin are among the remains preserved.

Chronologically-accumulated sediments that are undisturbed and laminated are most useful for close-interval paleolimnological analysis. Laminated sediments most often occur in lakes with a permanent oxygen deficit in the bottom waters (meromictic, or nearly so). Anoxia is perpetuated by the lack of turnover of deep waters, thus preventing turbulence and the establishment of organisms that would otherwise cause bioturbation (Saarnisto 1986). In these lakes, dating by counting varves (annual sets of laminae) is often possible (Leavitt et al. 1989; Simola 1979).

Fine temporal resolution over short time periods can be achieved in the absence of laminated sediments (Dixit et al. 1989), but is more difficult. One of the four lake basins cored for this thesis research, Annette Lake, had unlaminated sediments except for a single wide brown band of higher organic content. Another of the lakes, Peanut Lake (Treated basin), had an 11.5 cm unlaminated interval probably caused by a "slump". Resolving the chronology of these sediments will be discussed in the ensuing thesis chapters.

Freeze-coring

The method most used for close-interval sampling to reconstruct recent history is usually some variation of the freeze-coring device originally designed by Shapiro (1958). I used a "rocket" or "frozen-finger" corer (Fig. I-3; designed by P.J. Curtis, constructed by Nestor Lefaut, Dept. of Biological Sciences, University of Alberta; O'Sullivan 1983) consisting of a hollow aluminum cylinder that was filled with a slurry of dry ice and ethanol or methanol, and with a small vent at the top to allow the escape of CO_2 exhaust. The corer is lowered and retrieved by a rope attached to the top. It is placed into sediments at the deepest site in the lake and allowed to

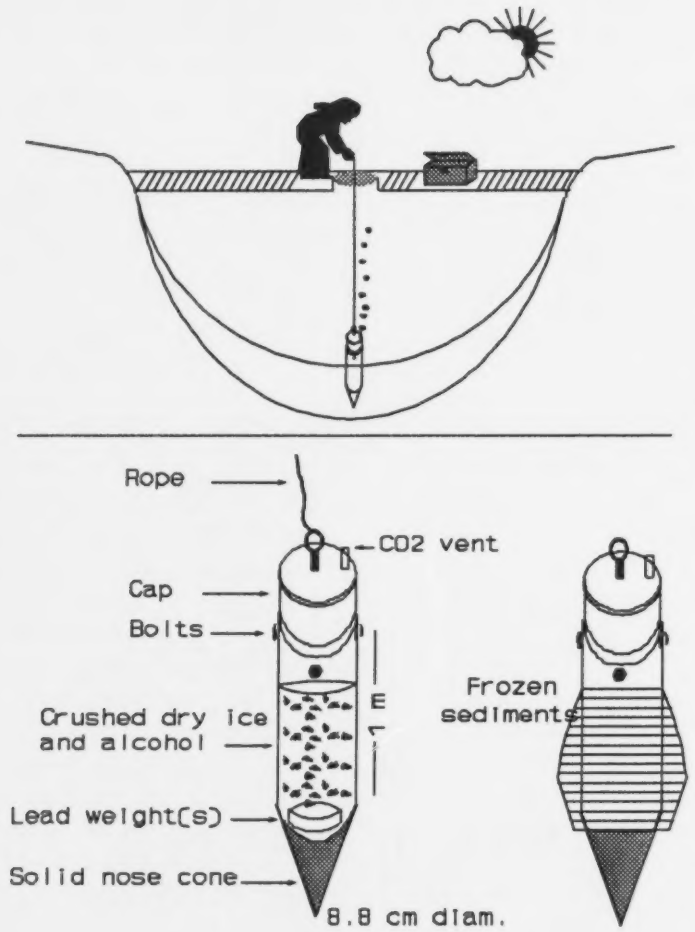


Figure I-3: Graphical depiction of freeze-coring procedure, and freeze core design.

equilibrate for ~12 minutes, freezing sediments about 2 cm in thickness on the *outside* of the tube. Once the core is back at the surface, the slurry inside is replaced with lake water or warmed water that allows the frozen sediments to be removed as an intact cylinder. Frozen cores are wrapped and returned from the lake in a cooler of dry ice. For the detailed freeze-coring and subsampling methodology, see Appendix B.

Other freeze-coring devices in use may be box-shaped (Huttunen and Merilainen 1978), or wedge-shaped (Renberg 1981) both with or without insulation on two or three sides. The insulation prevents freezing on those surfaces, producing a flat "slab" of frozen sediments. A recent innovation involves pumping liquid nitrogen at a constant rate into a core tube, allowing for 4-5 cm thicknesses of sediment to be collected (Renburg and Hansson 1993). Traditional freeze-corers usually collect 1.5-3

cm thicknesses of sediment on the outside of the corer wall, being limited by dry ice volume losses via unreplaced CO_2.

Chronology of lake sediment cores

Varve Counts

Varves are established by the presence of regularly-repeated colour bands (usually couplets or triplets), and often by repeated diatom bands (using tape-peels under magnification; Simola 1979). Lakes with annually laminated sediments are only found under certain specific circumstances but they are not as uncommon as once thought.

Perhaps the most important characteristic for the occurrence of lakes with laminated sediments is suitable lake morphometry. Lakes that are deep in relation to their surface area, are well-sheltered, with a relatively small drainage basin, and without significant inflows, are good candidates for having laminated sediments (Saarnisto 1986). While most lakes that have laminated sediments are <1 km in length, surface area <20 ha and depth of >15 m, many exceptions exist (some listed in Saarnisto 1986). In Alberta, examples of exceptions include Chatwin Lake (A_o=70 ha) and Amisk Lake (Length > 7 km; A_o=5.15 km^2).

Varve counting is precise because unlike radiometric dating, it is independent of variable sedimentation rates (Anderson et al. 1985). When varves occur with other markers, such as a clay band from construction (Leavitt et al. 1989) or charcoal from forest fires (of known dates; Swain 1973), varve counting can be particularly accurate.

Pb-210

Pb-210, an isotope with a half-life of 22.3 years, is useful for dating lake sediments deposited in the past 150 years (Olsson 1986; Krishnaswami and Lal 1978). The ^{210}Pb dating method is based upon quantifying ^{210}Pb in sediments that is usually assumed to be supplied at a constant rate, mainly from atmospheric sources (Fig. I-4).

Most of the ^{210}Pb directly deposited from the atmosphere through wet precipitation and dry fallout results from the radioactive decay of ^{222}Rn escaping from the earth's crust (Jaworowski 1969). Rn-222, with a half-life of 3.8 days, is a gaseous daughter product of the much longer-lived ^{226}Ra which exists in most rocks, soils and sediments. The mean residence time of ^{210}Pb in the atmosphere is about 5 days (Krishnaswami and Lal 1978), with global average deposition rates on the earth's surface in the order of 0.02 $Bq.cm^2.yr^{-1}$ (Appleby and Oldfield 1983). The ^{210}Pb derived from atmospheric fallout is termed "unsupported ^{210}Pb" (Fig. I-4).

The unsupported component of ^{210}Pb is continuously supplemented with more ^{210}Pb within lake water and sediments by the gradual decay of *in situ* ^{226}Ra and daughter products (Olsson 1986; Fig. I-4). This "supported" ^{210}Pb or background activity, often assumed to be levels measured in sediments older than 150 years, is subtracted from total activity to obtain only the "unsupported" ^{210}Pb.

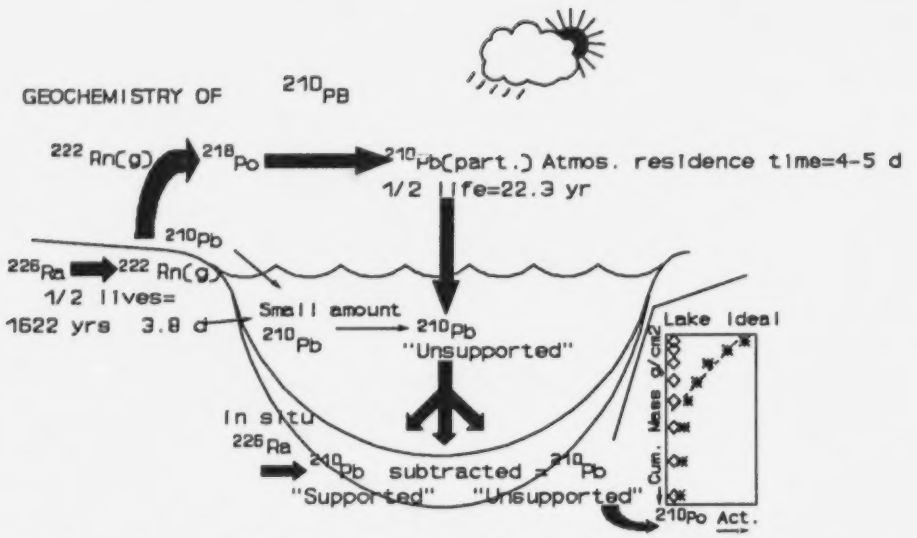


Figure I-4: Depiction of ^{210}Pb cycle in lakes with idealized graph of cumulative mass vs ^{210}Po activity.

Pb-210 Assays

The Constant Rate of Supply (c.r.s.) model used in this thesis, was originally devised by Goldberg (1963), and revised by Eakins and Morrison (1978). It assumes that the same amount of unsupported lead (A_x) is supplied per chronological unit. As with other isotopes, after time t, A_x has decayed to:

$$A_z = A_x e^{-\lambda t}$$

and is then buried at the depth z, with t=0 being the sediment-water interface. The decay constant (λ) for ^{210}Pb is 0.03114.yr^{-1}. If no mixing occurs and the sediment accumulation rate does not change, the distribution of ^{210}Pb activity vs depth in a sediment core is described by an exponentially declining curve (Binford 1990; Fig. I-4). Often mixing does occur, sediment accumulation rates do change, and the supported component of ^{210}Pb does not always equal a steady background as assumed, presenting some of the problems encountered in this assay. Problems are controlled by supplementing ^{210}Pb assays with other dating methods. Specialized equipment is required for ^{210}Pb dating, and as such, samples described in this thesis were analyzed by Dr. R. L. Flett, Flett Research Ltd., Winnipeg, MB, (Tel 204-667-2505).

Cs-137

Cs-137, with a half-life of 30 years, is one of many isotopes produced artificially as a consequence of nuclear weapons testing in the Northern Hemisphere. In 1957 the first pronounced increase in ^{137}Cs occurred, in 1960 there was a minimum, in 1963 the maximum, but by 1965 the global activity was about one-third of that in 1963 (Olsson 1986). Most artificial nuclides, including ^{137}Cs, were injected into the stratosphere from where they were removed to troposphere with a mean residence time of about 1 year (Krishnaswami and Lal 1978). Residence time in the atmosphere is similar to ^{210}Pb.

One of the main criticisms of ^{137}Cs in determining reliable sediment accumulations rates is reported post-depositional mixing, erosion, and redeposition (Longmore et al. 1983; Olsson 1986), which may mask the original delivery pattern to the sediments. Despite some mobility even in undisturbed cores, ^{137}Cs usually shows a prominent peak in northern hemisphere lake sediments representing years of highest fallout (1962-64; Jaakkola et al. 1983). As such it is a useful complement to other dating methods, and is particularly relevant for lakes studied in this thesis because they were treated with toxaphene at about the same time. Annette Lake sediments were analyzed for ^{137}Cs by Dr. Malcolm Stephenson, Atomic Energy of Canada Ltd, Pinawa, MB.

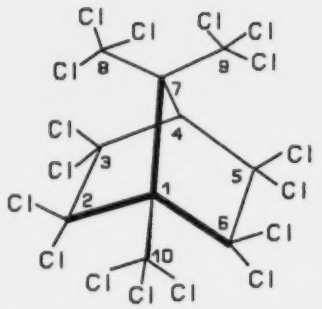
For my thesis research, sediments from Chatwin Lake and Peanut Lake(s) were laminated, and Annette Lake contained only a single wide lamination. The chronology of cores from each lake was established using two or more dating procedures; therefore, no one method of dating was wholly relied upon.

Toxaphene as an aquatic contaminant

One of the main problems my research addressed was the effect of toxaphene on aquatic ecosystems, both past and present. Toxaphene is a mixture of polychlorinated camphenes and bornanes that was first introduced in the United States in 1945 by Hercules Co. as Hercules 3956, a new insecticide to control a variety of insect pests. Its primary use was on cotton and other crops in the southern U.S., as well as for a cattle dip (Korte et al. 1979). Peak toxaphene use in the U.S. was during the early 1970's coincident with and as a replacement for banned DDT. Some physical, chemical and structural properties of toxaphene are given in Table I-2, with a depiction of its structure in Fig. I-5.

Toxaphene was also used by fisheries managers in Canada and the U.S. as a poison to extirpate undesirable fish prior to stocking salmonids. This practice was discontinued a decade or more prior to the eventual banning of toxaphene (early 1980's), when it was discovered that toxaphene was extremely persistent and remained toxic to stocked fish (Lee et al. 1977; Terriere et al. 1966) and invertebrates (Webb 1980; Larkin et al. 1970; Hilsenhoff 1971) for years after application (Saleh 1991). The longer-term effects and residue of toxaphene in lakes was not examined prior to my research. The nine lakes in Alberta that were treated with toxaphene between 1957 and 1962 are *Annette*, Moab, Dorothy, First of Five, Struble, Fish, *Peanut*,

Chatwin and Hasse Lakes[1]. Numerous other lakes in Alberta have been treated with rotenone[2] to extirpate fish from the 1940's to the present (see Appendix C).



Toxaphene skeleton

Figure I-5: Chair configuration of the basic toxaphene structure.

Several reviews of toxaphene usage, chemistry, toxicity, biochemistry, environmental residues, and residue analysis have been written (Saleh 1991; Bidleman et al. 1988; Ware 1988; Rice and Evans 1984; Pollock and Kilgore 1978). A toxaphene workshop was held 4 - 6 February 1993 in Burlington, Ontario resulting in an issue of Chemosphere on the analytical and environmental chemistry of toxaphene (Chemosphere 27(10) Nov. 1993). Interest in toxaphene has not waned with curtailment of its use in Canada and the U.S. because it is still a global pollutant that is transported through the atmosphere to be found in areas far from its original sites of application, including the Canadian Arctic. Toxaphene is still used in Mexico, Germany, eastern Europe, Russian countries, India and many African countries (Saleh 1991). Unfortunately, many studies are prevented or hindered by the complexity and extremely high cost of analysis of this 177+ congener compound. As Chapter IV of this thesis describes, extensive alteration of the parent compound usually occurs, adding to the difficulty of identifying residual chlorobornanes as toxaphene. Dr. Derek Muir, Norbert Grift and Gary Stern, at the Freshwater Institute, DFO, 500 University Crescent, Winnipeg, MB. were responsible for all analytical procedures during the analyses of chlorobornanes described in this thesis. Dr. Muir's telephone number is 204-983-5168.

Invertebrates quantified in this study

The invertebrates that will be discussed in this thesis are Cladocera (Daphniidae, Bosminidae and Chydoridae), and Diptera larvae (Chironomidae and Chaoboridae). These organisms were hypothesized to be affected by toxaphene application and/or fish stocking and are representative of the various spatial zones within temperate lakes. *Daphnia* spp., *Bosmina* spp. are generally planktonic, Chydoridae are mainly meiobenthic in the littoral zone, Chironomidae are benthic (littoral and profundal), and *Chaoborus* spp. are benthic but also migrate through the

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[1] Lakes in italics were studied in this thesis research.

[2] A plant-derived fish poison that is less persistent than toxaphene.

water column (generic habitat summary, Fig. I-6).

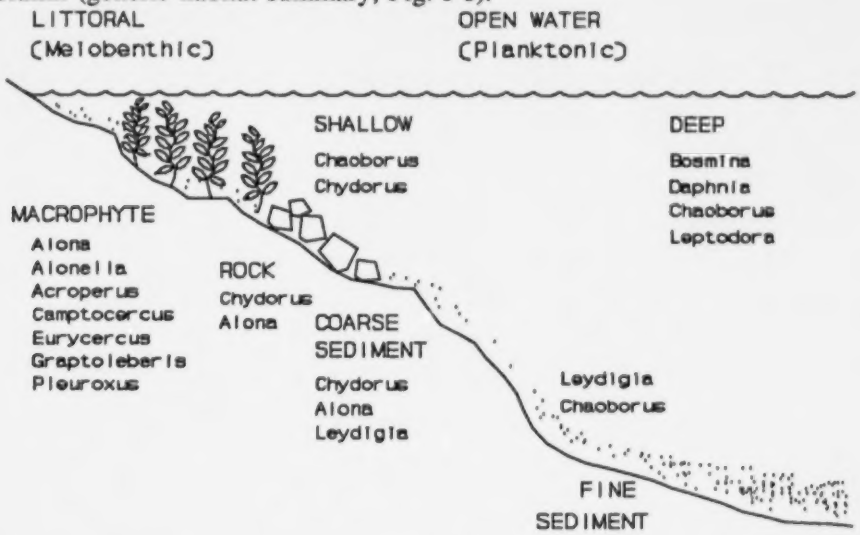

Figure I-6: Depiction of typical habitat of invertebrates quantified during this research (Hann 1989). Chironomids (not shown) are benthic in littoral and profundal zones.

Enumerated remains of these organisms in paleolimnology can be presented as (1) relative abundance -- percentage of the total at each level, (2) concentration -- numbers per gram of dry sediment, or (3) accumulation rate -- remains per $cm^3.yr^{-1}$. In this thesis, I each of these types of presentation. This will be discussed further in the relevant chapters.

Planktonic Cladocera

Daphnia spp. and *Bosmina* sp. are among the few microcrustacean zooplankters that are consistently represented in sediments. For this study, daphnids were enumerated and identified by their postabdominal claws (claw pair = 1 individual), and bosminids by their headshields or carapaces (whichever was most abundant, Hann 1989).

Unfortunately, daphnids are sometimes difficult to identify to species because the claws of some species are not unique. During my study, the claws of *D. pulex* were easily distinguished, but those of *D. rosea* could not be differentiated from *D. galeata*, both of which were identified in contemporary samples from Peanut Lake. Nevertheless, *D. pulex* represents a large-bodied zooplankter, *D. rosea/galeata* represents an intermediate size, and *Bosmina* represents the smallest size. This fact has important implications for food-web interpretations to be discussed in the following chapters.

Littoral Cladocera

Remains of Chydoridae are well preserved in sediments and are identifiable to genera or species, particularly with a reference collection of whole animal exuviae from the region of study (Dodson and Frey 1991; Hann 1989). Their chitinous headshields, carapaces or postabdomens become integrated before being incorporated within the sediments.

The quantity of these vegetation or mud-associated organisms (Fig. I-6) is greater toward shore than in the deepest part of the lake, but the relative abundance by species is the same (Mueller 1964). It would not be appropriate to compare accumulation rates of littoral cladocerans like Chydoridae directly to accumulation rates of planktonic cladocerans (Daphniidae, Bosminidae) because the most abundant remains of each are found nearest to their original habitat. Hence, any relative abundances were calculated separately.

While a few studies have attempted to quantify the habitats and spatial arrangements of chydorids in relation to chemical and physical factors (eg. Goulden 1971; Whiteside et al. 1978; Cotten 1985), some paleolimnological interpretations are weakened by a lack of comprehensive knowledge of the ecology of this group. However, these organisms are among the most taxonomically diverse of invertebrate remains found in cores, adding breadth to the "before, during, and after" nature of my reconstructive study. Some information was gained about their response and community reorganization following pesticide application.

Chironomidae and Chaoboridae (Diptera)

The larval forms of chironomids and *Chaoborus* spp. are aquatic and have head parts that preserve well in sediments. The mandibles of both groups, plus the lingua of chironomids, are most commonly used in paleolimnological analyses. Specialists normally will identify chironomid lingua to the generic level (Walker 1987; Walker and Mathewes 1989; Warwick 1989, 1992), while *Chaoborus* mandibles are often easily keyed to species (Borkent 1981; Uutala 1990).

In this thesis, the presence of *Chaoborus americanus*, *C. flavicans* or *C. punctipennis* indicated important differences in the fish communities from toxaphene-treated lakes. Chaoborids are often used to infer the historical status of fish in lakes (e.g. acidified lakes, Johnson et al. 1990) because their presence or absence is closely linked with planktivorous fish. *C. americanus* is susceptible to fish predation because it does not migrate vertically (Pope et al. 1973). Thus, the presence of *C. americanus* in sediment cores usually indicates that the lake did not support planktivorous fish at the time the organism existed in the lake. The other species co-exist with fish predators because they migrate toward darker waters or sediments during the daylight hours. All species are predacious on smaller invertebrates, notably *Bosmina*, sometimes partly explaining the abundance of other members of the aquatic food web (See Chapter II).

I report historical changes in total chironomids in toxaphene-treated lakes. I originally surmised that sediment-associated organisms might be adversely affected by toxaphene for a longer period than non-sediment associated organisms (because

toxaphene is particle-reactive). This theory was not supported with respect to total chironomids. A future project that considers generic separation might reveal the sensitivity of some taxa to toxaphene, food web changes or other variables.

Plant pigments

Because toxaphene was mainly designed as an agricultural pesticide (reviewed by Bidleman et al. 1988; Saleh 1991), primary producers are not directly affected by toxaphene except at very high concentrations (0.1-1.0 $mg.L^{-1}$, *Scenedesmus* sp.; Stadnyk et al. 1971). However, algae do respond sensitively to biological changes that may be indirectly imposed, such as food web or nutrient changes (e.g. Leavitt et al. 1989), or to physical changes like salinity and climate (Hickman and Schweger 1993).

Sedimentary pigments have been used in paleolimnological studies since the 1950's (Vallentyne 1955; Sanger 1988). While traditional productivity studies usually focus only on phytoplankton, pigments in lake sediments actually store a compilation of all primary producers including macrophytes, net and nanno-plankters, as well as photosynthetic bacteria (Sanger 1988).

The biggest problem with plant pigments is differential preservation (see reviews by Swain 1985, Sanger 1988, Leavitt 1993). Pigments are especially sensitive to light, heat, oxygen, acids, and sometimes to alkali (Davies 1976). Bias may result from rapid and selective degradation of certain pigments during sinking and burial (Leavitt 1993). Of relevance to my research, deep water sediments usually lack light and oxygen, and are very cold. Photo-oxidation and biological degradation would be expected to be lessened once the pigments reached the deep water sediments (Leavitt 1993).

In my research, I examine the response of 10-12 pigments in the eutrophic Chatwin Lake and the oligotrophic Annette Lake. Results are reported as $nmoles.g^{-1}$ dw (dry weight). The pigment results are combined with chydorid analyses from these lakes, representing Chapter III.

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Table I-1. List of principal organic and inorganic remains quantified in paleolimnological studies.

SEDIMENT SAMPLED FOR	PRESERVED	REASON FOR COLLECTION
Plant pigments (phytoplankton)	- resistant pigments - low degradation in anoxic cond'n	- chemical, nutrient status and food web change
Diatoms (Bacillariophyta)	- silica frustules - numerous, diverse (up to 250 species)	- Climate change, water level change - sensitive pH change
Chrysophyta	- 1 to 15 species - silica scales - stomatocysts	- high nos. in nutrient-poor lakes - planktonic (unlike many diatoms) - sensitive pH change
Pollen & Conifer needles (terrestrial)	- refractory	- change to terrestrial system/watershed - vegetation change (fire, flood, land cleared)
Aquatic macrophytes Spores, seeds	- if very abundant - lot of sed. req'd	- similar to pigments - water level change
Cladocera (planktonic & littoral)	- chitinous claws & exoskeleton	- food web change, toxic responses
Dip era (chaoborids, chironomids)	- head capsules, mandibles	- O_2 change, temperature change, deformities due to chemicals; food web change
Porifera (freshwater sponges)	- gemmules, spicules - need lg. vol of seds. (~20 cm^3)	- long-term change: climate, pH
Testate amoebae (Protozoa)	- tests	- peatland hydrologic change
Ostracodes	- calcitic valves (shells)	- water level, salinity, O_2, and Temp. change
Fungi	- spores	- water level, pH change
Larger organisms: molluscs, beetles, mites, fish scales	- less abundant - large vol. of seds required	- long-term change only
Chemicals	- charcoal, clay, organochlorines, metals	- fire, flood, contamination, etc.

Table I-2. Some chemical, physical and toxicological properties of technical toxaphene (from reviews by Rice and Evans 1984; Saleh 1991; El-Sebae et al. 1993)

(Note: >32000 theoretical isomers, each has its own characteristics; mixtures vary in composition; Vetter 1993)

Avg. empirical formula	$C_{10}\ H_{10}\ Cl_8$
Avg. molecular weight	
Parent compound	414 $g.mol^{-1}$
Heptachlorobornanes	379 $g.mol^{-1}$
Vapor pressure	3×10^{-7} mm Hg at 20°C 1×10^{-6} mm Hg at 25°C
Water solubility	3-740 $\mu g.L^{-1}$ reported
log octanol-water coeff. (Log K_{ow})	6.44
Mean specific gravity	1.630 $g.mL^{-1}$ at 25°C
Henry's Law Constant	1.7×10^{-6} atm $m^3.mol^{-1}$
Toxicity (ppb)	
LC_{50}, 96 h, most freshwater fish	1.6-100 $\mu g.L^{-1}$
LC_{50}, 96 h, invertebrates	1.3-30 $\mu g.L^{-1}$
Human carcinogenicity, oral dose	1.131 $mg.kg^{-1}.d^{-1}$
Can. Health & Welfare consumption guide	0.2 $\mu g.kg^{-1}.d^{-1}$
Recommended "no effects" H_2O conc.	0.008 - 0.013 $\mu g.L^{-1}$
U.S. production 1964-82	~233,700 tonnes
World use 1946-74	~409,000 tonnes

II. LONG-TERM INVERTEBRATE COMMUNITY RESPONSE TO TOXAPHENE TREATMENT IN TWO LAKES: 50-YEAR RECORDS RECONSTRUCTED FROM LAKE SEDIMENTS.[3]

Introduction

Toxaphene is a mixture of polychlorinated camphenes (PCC) that was once widely used as a piscicide and an agricultural pesticide in both Canada and the United States. Now banned for most uses in North America, toxaphene is still used in other parts of the world. Toxaphene and its residues are among the persistent organochlorines that are considered global pollutants, because they are carried in the atmosphere and are found in ecosystems far from the original sites of utilization (Rice and Evans 1984; Muir et al. 1988; Van der valk and Wester 1991). During the 1950's and 1960's, numerous provincial and state agencies considered toxaphene a less expensive and more lethal alternative to rotenone for extirpating undesirable fish from lakes prior to stocking with various species of trout ("lake rehabilitation"; Cumming 1973).

Toxaphene application to lakes has caused both direct and indirect ecosystem damage. Monitoring studies revealed poor survival of stocked trout for many years (Terriere et al. 1966; Webb 1980) and bioaccumulation by aquatic plants and animals (Terriere et al. 1966). There were also reports of detrimental effects on non-target organisms in the lakes such as chironomids (Cushing and Olive 1957), cladocerans, amphipods (Larkin et al. 1970), three species of *Chaoborus* (Hilsenhoff 1971) and *Chaoborus punctipennis* (Webb 1980). The time for recovery of invertebrates following toxaphene application varied from many months (Cushing and Olive 1957; Hooper 1959) to several years (Larkin et al. 1970; Hilsenhoff 1971; Webb 1980). Unfortunately, monitoring programs were relatively scarce, and either too brief or not comprehensive enough to evaluate the longer term effects of toxaphene on lacustrine communities.

In addition to the effects of toxaphene, the replacement of a native and diverse fish community by a single salmonid population would be expected to modify the invertebrate communities in lakes. Any significant change in fish density and/or feeding habits could alter the types, sizes and abundances of food-base organisms (Anderson 1970; Carpenter et al. 1985; Leavitt et al. 1989). With few vertebrate predators (planktivores) present, large invertebrate predators and large herbivores (like some daphnids) usually increase causing reductions in small crustaceans (Brooks and Dodson 1965; Shapiro and Wright 1984). Further, when lakes have few or no planktivorous fish, *Chaoborus americanus* often becomes the dominant chaoborid, because it does not migrate downward into darker waters during the day to avoid predation by fish (Borkent 1981) and because they can outcompete smaller chaoborids

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[3] A version of this chapter has been published. Miskimmin & Schindler 1994. Can. J. Fish. Aquat. Sci. 51: 923-932.

(Pope et al. 1973; Von Ende 1979; Uutala 1990). Even assuming that trout fry diets were similar to some native planktivores (Scott and Crossman 1973), predation pressure on invertebrate prey would be constrained by the absence of natural recruitment of fish and dependence on the stocking success of hatchery trout.

Close-interval sampling of lake sediment cores can provide long-term records of many organisms residing in and around lakes (Frey 1988). Lake sediments sometimes accumulate in undisturbed laminae that permit accurate temporal analyses of invertebrate and plant communities. An example of the utilization of chaoborid and chironomid remains from sediment cores was the reconstruction of the historical status of fish populations (acidified lakes in Ontario, Johnson et al. 1990), one of the aims of my study. I quantify chironomids, chaoborids and cladocerans which have identifiable body parts that preserve well in sediments. When the chronology of sediment deposition can be established, these members of the aquatic community can be enumerated, and can supplement existing limnological data.

Here I examine the response to toxaphene application and stocking with a non-native fish species on total chironomids, *Chaoborus* spp. and planktonic Cladocera in a mesotrophic and a eutrophic lake in central Alberta, Canada. I compare the response in the lake that received a low toxaphene dose to one with a higher dose, and contrast the results with a lake basin that was not treated. My objectives were to establish a long-term record of some members of the invertebrate community prior to 1961-62 toxaphene applications, determine any patterns in toxic response, and examine the recovery of the communities in the 30 years following disturbance.

Materials and Methods

Study Sites

The central Alberta lakes were chosen for coring because of their common history of toxaphene treatment and trout stocking, their suitable morphometry for accumulating laminated sediments (small, deep, seepage lakes), and differences in productivity and chemical characteristics (Table II-1). Both lakes are in the Boreal Mixedwood Ecoregion (*Populus tremuloides* dominated). The lakes have a sparsely documented chemical and fisheries history, most of which was gathered by Alberta Department of Fish and Wildlife, and is available to researchers (referred to hereafter as AFW files).

Eutrophic Chatwin Lake (Table II-1) has two cattle farms (est. prior to 1952, and expanded in the 1980's) and a golf course in its otherwise forested watershed. Prior to toxaphene treatment (18.4 $\mu g.L^{-1}$) in 1962, the fish community consisted of northern pike (*Esox lucius*), yellow perch (*Perca flavescens*) and brook stickleback (*Culaea inconstans*; AFW files; Fig. II-1). Chatwin Lake was stocked in 14 of 28 years between 1964-1992 with a total of 980,000 hatchery rainbow trout (*Oncorhynchus mykiss*; mean of 1,100 $fish.ha^{-1}$ per stocking event). Survival of stocked trout has been very poor, and other fish species are absent (AFW files).

Chatwin Lake had clearly laminated sediments in all cores that were collected. At present, this lake has a high density of littoral and pelagic Amphipoda (*Gammarus lacustris*, *Hyalella azteca*). The order of numerical abundance of zooplanktonic

organisms sampled in mid-summer 1992 with a 64 µm mesh plankton net follows: *Asplanchna* (Rotifera, Ploima) > *Daphnia pulex* (Cladocera) = *Acanthodiaptomus denticornis* (Calanoida) > *Chaoborus flavicans* (Diptera) > *Keratella* (Rotifera, Ploima) > *C. americanus* >> *Ceriodaphnia* sp. (Cladocera).

Mesotrophic Peanut Lake lake has a cattle farm (est. 1911) in the eastern portion of its watershed but is otherwise relatively undeveloped. The lake is comprised of two basins that were joined prior to toxaphene treatment, but permanently divided in the same year as toxaphene treatment by construction of an earth berm across the narrows (Fig. II-1). Prior to treatment, the lake contained walleye (*Stizostedion vitreum*), yellow perch, and various small cyprinids (AFW files). Some walleye and yellow perch were transferred from a nearby lake to Peanut Lake in the 1930's (AFW files), although a clear record of whether either of these taxa was present prior to this does not exist. Toxaphene (7.5 $\mu g.L^{-1}$) was applied to remove all fish from the north basin in 1961, leaving the south basin untreated.

The treated basin of Peanut Lake was first stocked in August 1965, and has been stocked annually since 1967 with hatchery rainbow trout (total of 330,000 fish; mean of 600 $fish.ha^{-1}$ per stocking event). It also currently supports fathead minnow (*Pimephales promelas*), brook stickleback and a few walleye (a single 1 kg specimen was caught by the author in 1991). These species may have been re-introduced by anglers (D. Berry, Alberta Fish and Wildlife, 5th floor, 9920-108 St., Edmonton AB, T5K 2M4, pers. comm.). No current records for fish in the untreated basin of Peanut Lake exist. The untreated basin was thought to maintain a yellow perch population in the 1950's and early 1960's, prior to and shortly after the basins were divided (AFW files). Fish are probably depleted or absent now in this smaller basin because oxygen is occasionally reduced to extremely low levels (0 - 0.5 $mg.L^{-1}$) in the winter under ice (AFW files).

The treated basin of Peanut Lake has laminated upper sediments with the exception of an 11.5 cm interval of unlaminated material (~9.5-21 cm depth, referred to hereafter as a "slump"), possibly from earth introduced into the lake during construction of the berm between the basins just after toxaphene treatment (Fig. II-1; Don Hove, County of Barrhead Public Works Dept., Barrhead, Alberta; pers. commun.). Two other physical markers were useful in matching depths between core sections: 0.5-1 cm light-coloured bands at 24 cm and 30 cm. The untreated basin has laminated sediments that are uninterrupted by mixed intervals as occurred in the treated basin. The order of numerical abundance of zooplanktonic organisms sampled in mid-summer 1992 in the treated basin with a 64 µm mesh plankton net was small cyclopoids (*Diacyclops* sp.) = calanoids (*Hesperodiaptomus* sp.) > *Daphnia pulex* = *Daphnia rosea* > *Bosmina* (Cladocera) > rotifers.

Core Collection

Two or three sediment cores were collected by freeze-coring (O'Sullivan 1983) at the deepest site on each of the 3 lake basins (Chatwin; Peanut Treated and Untreated basins). Distinct laminations verified that sediments were relatively undisturbed by the coring process. The cores were wrapped in aluminum foil, returned to the laboratory on dry ice, and stored at -10°C for further use. Cores were quartered lengthwise with a band saw, the exterior cleaned with a woodplane to remove contaminated surfaces, and thawed or freeze-dried before sampling. Sections of cores were analysed for cladoceran and dipteran macrofossils, organochlorines, ^{210}Pb chronology, and organic content. Because all analyses could not be done on individual quarter sections, a total of 4 or 5 quarter sections for each basin were used to complete the study. Between-section depth correlation was achieved by matching analogous laminae or other markers such as the distinctive light-coloured bands.

Dating and Organic Content

A combination of varve estimates (Chatwin Lake), physical markers, ^{210}Pb chronology (all 3 basins), and toxaphene analyses (the two treated basins) were used for dating sediments. Varves (annual sets of laminae) in Chatwin Lake were distinguished as regularly repeated colour bands, and were counted independently by two individuals. ^{210}Pb chronology was established by sampling 2-5 mL of sediments per sample from a thawed core, and assaying by the constant rate of supply model described by Eakins and Morrison (1978).

Toxaphene was determined on freeze-dried 0.8 to 1.0 cm slices of a quarter section. The slices were made by band sawing a frozen section, and were individually prepared (while frozen) by removing inner smeared surfaces and outer contaminated edges using a stainless steel knife. Analyses were completed on freeze-dried samples by electron capture detector gas chromatography (Varian 6000) as described by Muir et al. (1988). Toxaphene results were verified by negative chemical ionization mass spectrometry in selected-ion mode. Toxaphene maxima are used here only to confirm the year and depth of toxaphene application.

Organic content, defined as loss on ignition (LOI), was measured in core sections from the two treated lakes. Sediments were lyophylized (Virtis Freezemobile 6) for 24 h. This process left a 4 mm freeze-dried zone over a frozen base for the full length of the cores (approx. 20-30 cm). Sections of the dried material at 0.5 cm intervals were subsampled and weighed. LOI was determined by weight difference before and after burning at 550°C for 1.5 h.

Cladocerans

Samples were taken at 0.5 to 1.0 cm intervals from a thawed core section. Following the general procedure of Frey (1986), 1 mL of wet sediments was added to 15 mL of 10% KOH, gently heated, and occasionally swirled for 5 h. This period was adequate to deflocculate most particles in samples from these lakes. Supernatant KOH was decanted and the sediments diluted with distilled water at least three times. The final volume was brought to 5 or 10 mL and subsampled to slides (50 µL per slide)

using glycerin jelly stained with lignin pink as a mounting medium (Hann 1989). A Nikon phase contrast microscope was used to identify and enumerate *Daphnia* sp. and *Bosmina* remains (also Chydoridae: data not shown here) from four slides (200 µL), or until counts exceeded 150 per sample. Because *Daphnia rosea* are found in recent plankton samples, but have postabdominal claws that are not unique, claws of the type are reported as this species. Note that *D. rosea* are not distinct from *D. galeata mendotae* based on claw morphology. *Daphnia galeata mendotae* were identified in archived samples from Peanut Lake collected in the early 1980's by University of Alberta staff. Data are reported as accumulation of pairs of *Daphnia* claws or *Bosmina* headshields representing individuals.$cm^{-2}.yr^{-1}$. Identification of remains was based on Brooks (1959), Hann (1989), and Pennak (1978).

Dipteran Macrofossils

Three millilitre samples were taken from a thawed core section and deflocculated with 20-25 mL of 10% KOH similar to the cladoceran procedure. Invertebrate remains in the slurry were concentrated onto a 93 µm mesh, and rinsed into a plankton counting tray. No attempts were made to quantify any remains that passed through the mesh. These would be mandibles from the unidentifiable earliest instars for this group. *Chaoborus* sp. mandibles and total chironomid head capsules were enumerated using a dissecting microscope. *Chaoborus* species were identified based on the mandible key of Uutala (1990). Results are reported as accumulation of mandibles (chaoborid) or head capsules (chironomid).$cm^{-2}.yr^{-1}$.

Results

Dating

Accurate historical reconstruction of events in the two treated and one control lake basins was possible with the combined dating techniques of ^{210}Pb, toxaphene analyses, and varve counts (where possible). All sediment dating results are given on a dry weight basis.

The ^{210}Pb profile (Fig. II-2), varve counts and a toxaphene maximum (1600 $ng.g^{-1}$) in Chatwin Lake confirm the sediment depth of the 1962 treatment at 11.5 cm. Sediments have accumulated in this eutrophic lake at 31.6 ± 5.7 $mg.cm^{-2}.yr^{-1}$ for the period of record and were well laminated throughout the length of the cores.

Pb-210 profiles for Peanut Lake indicate an average sediment accumulation rate of 20.6 ± 1.8 $mg.cm^{-2}.yr^{-1}$ for the treated basin (Fig. II-2), and 18.4 ± 5.0 $mg.cm^{-2}.yr^{-1}$ for the untreated basin (Fig. II-2). Dating by varve counts in the treated basin cores was not possible because of the 11.5 cm slump (between 9.5-21 cm). The length of the slump was removed for the purposes of ^{210}Pb dating because it accumulated very quickly and independently of the true sediment accumulation rate in the lake. The depth of the toxaphene maximum of 500 $ng.g^{-1}$ coincided with ^{210}Pb estimates of the 1961 treatment depth (below the slump) at approximately 21 cm. The same year is represented at approximately 9.3 cm in the untreated basin.

Organic Content

The organic content (defined by LOI) of sediments in Chatwin Lake averaged 45.1 ± 4.0%, and in Peanut Lake (treated basin) averaged 29.8 ± 8.2% over the past 40-50 years (Fig. II-3). While sediment organic content in Chatwin Lake did not vary systematically, organic content in Peanut Lake increased substantially from the pre-toxaphene years (<1961: 23.7 ± 2.9%) to the post-slump years (>1962: 39.8 ± 4.3%).

Invertebrate Communities Prior to Toxaphene Treatment (1940-1961 or 1962)

Prior to toxaphene treatment, *Bosmina* and chironomids were the most abundant invertebrate remains found in Chatwin Lake sediments (Fig. II-4a). During the 1940's and again in the late 1950's, large herbivores (*Daphnia* spp.) were relatively abundant, although *Bosmina* was the dominant cladoceran in all pre-treatment samples examined. Large numbers of *Chaoborus flavicans* were present in Chatwin Lake for a few years in the early to mid-1950's.

From 1940 through 1960, Peanut Lake supported low abundances of the invertebrates examined in this study (Fig. II-4b). *Bosmina* was the dominant cladoceran in both the treated and untreated basins (the basins were not permanently divided during this period). *C. flavicans* was moderately abundant in both basins; however, chironomids accumulated at relatively higher rates in the smaller (untreated) basin (Figs. II-4b and c).

Invertebrate Changes Immediately Following Toxaphene Application (1961-1964)

Permanent changes in the planktonic invertebrate community composition occurred in Chatwin, but not in Peanut Lake following toxaphene application.

In Chatwin Lake, *Bosmina* was dominant prior to treatment, but numbers were reduced by 88% at the time of toxaphene treatment (Fig. II-4a). A short-term increase (1-2 yr) in *D. rosea* occurred about the time of toxaphene treatment, while *D. pulex* was unchanged. No change in total chironomid accumulation was detected in sediments representing the year of toxaphene treatment. Chaoborids were found at low levels both shortly before and after treatment in Chatwin Lake.

In contrast, in Peanut Lake *Bosmina* increased shortly (1-2 yr) after treatment. No such increase occurred at this time in the untreated basin, where instead, *D. rosea* commenced a steady increase in number (Figs. II-4b and c). Because daphnids, chaoborids and chironomids were present at low abundances in the treated basin of Peanut Lake prior to treatment (Fig. II-4b), toxic effects were not detectable.

Post-toxaphene Changes (mid-1960's to 1990)

Long-term changes in the invertebrates following manipulation of Chatwin and Peanut Lakes exhibit some similarities, including changes in dominance from small cladocerans to large ones (*Bosmina* to *Daphnia*, and/or small *Daphnia* sp. to large), and increases in invertebrate predators like *Chaoborus spp.* (Figs. II-4a and b). Significant increases in numbers of *Chaoborus* spp. did not occur until the late 1960's (Peanut, Fig. II-4b) to early 1970's (Chatwin, Fig. II-4a) despite the poor survival of trout throughout most of the 1960's.

In Chatwin Lake, an increase in *Chaoborus americanus* coincided with the elimination of *Bosmina* (already depleted by toxaphene). Chironomids and *D. pulex* were relatively stable since before the treatment, and *C. flavicans* never again reached the high numbers noted in the 1950's (Fig. II-4a). In contrast, in the treated basin of Peanut lake, all taxa considered have increased from the late 1960's onward to their highest levels in the 50-yr record (Fig. II-4b). *C. flavicans* became the dominant chaoborid and *Bosmina* was well represented in samples from Peanut Lake (unlike in Chatwin Lake). Note that most of the abrupt changes occurred after the slump of 1962 (year after toxaphene treatment) in the treated basin of Peanut Lake (Figs. II-3 and II-4b).

Daphnia rosea and *D. pulex* were rare in both the treated and untreated basins before treatment (and basin division). After the 1961 toxaphene treatment, increases in the small *D. rosea* preceded increases in the larger *D. pulex* by several years in both basins. Increases in both species of *Daphnia* and in *Chaoborus* occurred in the mid-1960's in both the treated and untreated basins. During the 1970's, small planktonic cladocerans, *Bosmina* and *D. rosea* were more abundant than *D. pulex* in both basins. During the 1980's, *D. pulex* became co-dominant with *D. rosea* in the treated basin of Peanut Lake, but remained at lower levels than the smaller cladocerans in the untreated basin.

Discussion

Toxaphene Effects

The reported poor survival of stocked rainbow trout in both toxaphene-treated lakes for many years after treatment did not occur in rotenone-treated lakes in Alberta and initiated concerns about residual toxaphene toxicity to trout (AFW files). Although it is not uncommon for small lakes in Central Alberta to winterkill, oxygen depletion was not usual in the treated basins of Peanut and Chatwin Lakes (AFW files), making residual toxaphene a conceivable problem. The failure of trout to survive in toxaphene-treated lakes in other areas was attributed to consumption of toxaphene-contaminated food organisms (Johnson 1966; Schoettger and Olive 1961). In addition to acute toxicity, toxaphene bioconcentrates by several orders of magnitude in food chains (e.g. 10^4 over water concentration for trout; Eisler and Jacknow 1985). Residual toxicity of toxaphene in treated lakes has not been reported to extend for more than a decade. Thus, while toxaphene might have caused residual toxicity problems in the 1960's, the reason for poor trout survival in the 1970's and beyond, despite intensive stocking in these prairie lakes, is unknown.

Stronger effects of toxaphene to invertebrates in Chatwin Lake than in Peanut Lake (Figs. II-4a and b) may be the result of the higher concentration of toxaphene used in Chatwin Lake (Fig. II-1). The concentration of toxaphene in Peanut Lake (7.5 $\mu g.L^{-1}$) was one of the lowest levels recommended to achieve a complete fish kill (Hooper 1959), while the Chatwin Lake dose was three times higher.

Specifically, differences in *Bosmina* survival between lakes may have resulted from the higher toxaphene concentration used in Chatwin Lake. A recommended non-lethal concentration of 10 $\mu g.L^{-1}$ toxaphene for *Bosmina* (Novak and Passino 1986)

was exceeded in Chatwin but not in Peanut Lake. *Daphnia pulex* and *D. magna* are less sensitive (non-lethal concentrations of 80 and 100 $\mu g.L^{-1}$) to toxaphene than *Bosmina* (Novak and Passino 1986), perhaps explaining daphnid survival in Chatwin Lake. Further, the International Joint Commission of the United States and Canada (1977) recommended a standard of 8 $\mu g.L^{-1}$ toxaphene for protection of aquatic life. This standard was exceeded by several-fold in the case of Chatwin Lake, and suggests that a lethal dose of toxaphene may have initiated the continuous decline of *Bosmina*.

In Chatwin Lake, it is possible that residual toxaphene was toxic for *Chaoborus* for many years. This lake sustained only low populations of *Chaoborus* spp. larvae throughout the 1960's despite the close proximity of other water bodies as colonization sources. In Chatwin Lake, no fish except low numbers of stocked trout have been recorded since toxaphene treatment, diminishing vertebrate predation as a reason for low *Chaoborus* populations. In a Wisconsin lake that was treated with toxaphene, *Chaoborus* spp. failed to recolonize until 4 years later (Hilsenhoff 1971). In an Ontario study, where lake morphometry and treatment were very similar to Chatwin Lake (A_o=65 ha, Zmax=16 m, Toxaphene=15 $\mu g.L^{-1}$), *Chaoborus punctipennis* shifted from representing 58% of benthic invertebrate abundance to complete extirpation at all depths following toxaphene treatment (Webb 1980). Webb also noted the poor survival of stocked trout (splake), and concluded that toxaphene (not predation), caused the complete absence of *Chaoborus* for the entire 4 years of monitoring.

In Peanut Lake, it is impossible to distinguish the relative contributions of residual toxaphene and other factors for the poor recruitment of *Chaoborus* spp. through the decade after toxaphene treatment. The untreated basin is the only one of the three lakes studied in which *Chaoborus* increased during the 1960's (Figs. II-4 a-c). The untreated basin is very close (100 m) to the treated basin, making *Chaoborus* recolonization of the treated basin potentially quite high. Thus, residual toxaphene might at first appear to have been a cause for poor recruitment of chaoborids. However, in addition to receiving a lower toxaphene dose than Chatwin Lake, and having low populations of *Chaoborus* prior to treatment, it is possible that minnow and brook stickleback (abundant in the treated basin of Peanut Lake at present) were not completely eliminated, or were reintroduced soon after poisoning. If so, then continuous fish predation could also be considered a cause of low *Chaoborus* populations from pre-treatment years to present. I am not sure why a similar control was not exerted in the untreated basin. Unfortunately, except for the probability that few or no fish remain because of low oxygen concentrations (AFW files), no specific records of fish populations in the untreated basin exist. Specific knowledge of the fish populations in both basins of Peanut Lake would further elucidate the relative contributions of predation by fish, toxaphene toxicity and probably other variables on *Chaoborus* abundance.

In Chatwin Lake, total chironomid abundance was apparently unaffected by toxaphene application. Chironomids have been observed to become depleted but to increase more quickly than other invertebrates after toxaphene application (Stringer and McMynn 1958; Webb 1980), a response that was partly attributed to removal of benthivorous fish (Webb 1980). In another case, chironomids were absent for 9

months from samples in a lake treated with five times the toxaphene dose that Chatwin Lake received (Cushing and Olive 1957). Thereafter, they repopulated the lake. My subsamples for dipterans may combine remains from more than one year, because several laminae are usually required to make up the necessary sample size (3 mL). This would obscure short-term responses of dipterans that may have been affected for only 1 or 2 years, resulting in the conservative conclusion that total chironomid abundance was unchanged by toxaphene treatment.

It is possible that further taxonomic characterization of the chironomid fauna might reveal sensitivity of specific taxa. In his monitoring study in Ontario, Webb (1980) found that members of the subfamily Orthocladiinae, and *Chironomus cucini* only reappeared 4 years after toxaphene treatment, that *Phaenopsectra (Sergentia) coracina* and *Procladius freemani* recovered after 1 year, and one species (*Cryptotendipes casuarius*) that had not occurred in the lake before, appeared in the lake 2 years after treatment. He noted that overall chironomid abundance was reduced for only one season, and that significant increases occurred thereafter. Because chironomid head parts usually preserve well enough in sediments for generic identification (Walker 1987), further taxonomic work might reveal a genera-dependent response of chironomids in lakes that were treated with toxaphene.

Long-term (Post-toxaphene) Recovery

A long-term change from small to large invertebrates is expected when the abundance of planktivorous fish is reduced (Brooks and Dodson 1965; Shapiro and Wright 1984; Carpenter et al. 1985; Leavitt et al. 1989). Because large invertebrates replaced smaller ones in Chatwin Lake and large invertebrates increased greatly in both basins of Peanut Lake, (Figs. II-4 a-c), I infer reduced planktivory as the principal explanation. Reduced numbers of planktivores are consistent with government records that indicate poor trout catches in test nets despite intensive stocking in the two treated lakes (AFW files).

Low levels of zooplanktivory by stocked or reintroduced fish populations have also been observed in lakes that were treated with rotenone. For example, the shift to dominance by large-bodied zooplankton has occurred in other rainbow trout-stocked lakes that were first treated with rotenone (Anderson 1970; Leavitt et al. 1989). All except one crustacean species reached pre-rotenone abundances in about 3 years in two mountain lakes (Anderson 1970). Large herbivores apparently recovered immediately and remained dominant after rotenone treatment and during trout stocking in Paul Lake, Michigan (Leavitt et al. 1989).

One clue as to the possible presence of planktivores (briefly mentioned in the previous section) in the untreated basin of Peanut Lake is the absence of *Chaoborus americanus* in sediments since basin division (Fig. II-4c). *C. americanus* was detected in the 1940's in the untreated basin of Peanut Lake, and would be expected to reappear in the complete absence of predatory fish (Pope et al. 1973; Johnson 1990). *C. flavicans*, a species that does co-exist with planktivores (Johnson 1990) became extremely abundant in the untreated basin in the past 20 years suggesting a few planktivores may have persisted despite depleted oxygen during the winter. The

presence of re-established minnow and brook stickleback populations in the treated basin (AFW files) and this evidence of residual populations in the untreated basin, would likely explain many of the similarities found in invertebrate remains in both basins.

Increases in both the abundance of invertebrates (Figs. II-4b and c) and sediment organic matter (Fig. II-3) suggest that Peanut Lake became more productive from the 1960's onward. In contrast, in Chatwin Lake, chironomid abundance (Fig. II-4a) and percent organic matter did not vary much over the 50-year history, suggesting that productivity has not changed substantially in this lake during the period of study. The lack of change in organic matter in Chatwin Lake despite the much higher dose and sediment concentrations of toxaphene preclude implications of long-term toxicity to bacterial decomposers. Increased percent organic matter of sediments may be inferred as higher productivity because of either an increase in nutrient inputs or longer water residence times (Dillon 1975; Schindler et al. 1978; Whiteside 1983). Water residence times in similar small, seepage lakes in central Alberta are estimated to exceed 100 years (Mitchell and Prepas 1990), making it unlikely that altering this factor by even several years would contribute to changes in production. Increased nutrient loading may have been caused by the farming operation that encompasses about one-third of the shoreline of Peanut Lake and by additional public use of the treated basin in the past 20 years.

Predation by invertebrates may have contributed to the long-term depletion of the small-bodied herbivores in Chatwin Lake. *Daphnia rosea* were greatly reduced and *Bosmina* were eliminated coincident with rises in predatory *C. americanus* in Chatwin Lake during the 1970's (Fig. II-4a). This chaoborid is an effective predator on small zooplankton (Elser et al. 1987). In some cases, large populations of *Chaoborus* spp. have been known to decimate (Von Ende and Dempsey 1981), or at least strongly regulate (Yan et al. 1991) *Bosmina* populations. Clearly, *Bosmina* never recovered from toxaphene-induced depletion in Chatwin Lake, and probably was ultimately eliminated by intense invertebrate predation (Fig. II-4a, mid-1970's). Other explanations including competition or other factors cannot be applied because they are difficult enough to establish based on contemporary records, and are too speculative to infer from the sedimentary record.

In summary, the short-term responses to toxaphene treatment of the invertebrate communities in two treated lakes differed, probably mainly due to different toxaphene dosages. Toxicity was apparent for some organisms in the lake with a higher toxaphene dose, but was not detected in the lake with the lower dose. Long-term effects on invertebrates after treatment and stocking of the lakes were similar in many ways, and were probably the result of less intense planktivory after treatment, despite repeated stocking with rainbow trout.

The information gained from sediment cores from these lakes would otherwise have been lost because of the lack of contemporary monitoring data. The paleolimnological methods used in this study could easily be applied to other suitable lakes to reconstruct the effects of perturbations of many kinds.

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Table II-1. Characteristics of study lakes treated with toxaphene in 1962 and 1961.

	Chatwin Lake	Peanut Lake
Latitude	54°15'N	54°01'N
Longitude	110°51'W	114°21'W
Area	71 ha	24 ha Treated/5 ha Untreated[a]
Maximum depth	15.8 m	14 m [b]
pH	9.2	9.1
Conductivity	1400 $\mu S.cm^{-1}$	510 $\mu S.cm^{-1}$
Alkalinity	16.4 $meq.L^{-1}$	6.2 $meq.L^{-1}$
Total P	47 $\mu g.L^{-1}$	20 $\mu g.L^{-1}$
Total Dissolved P	37 $\mu g.L^{-1}$	9 $\mu g.L^{-1}$

[a] 1961: Treated Basin treated with toxaphene; Smaller basin untreated.

[b] Both basins are similar depths, other characteristics are approximate ice-free season values of the treated basin.

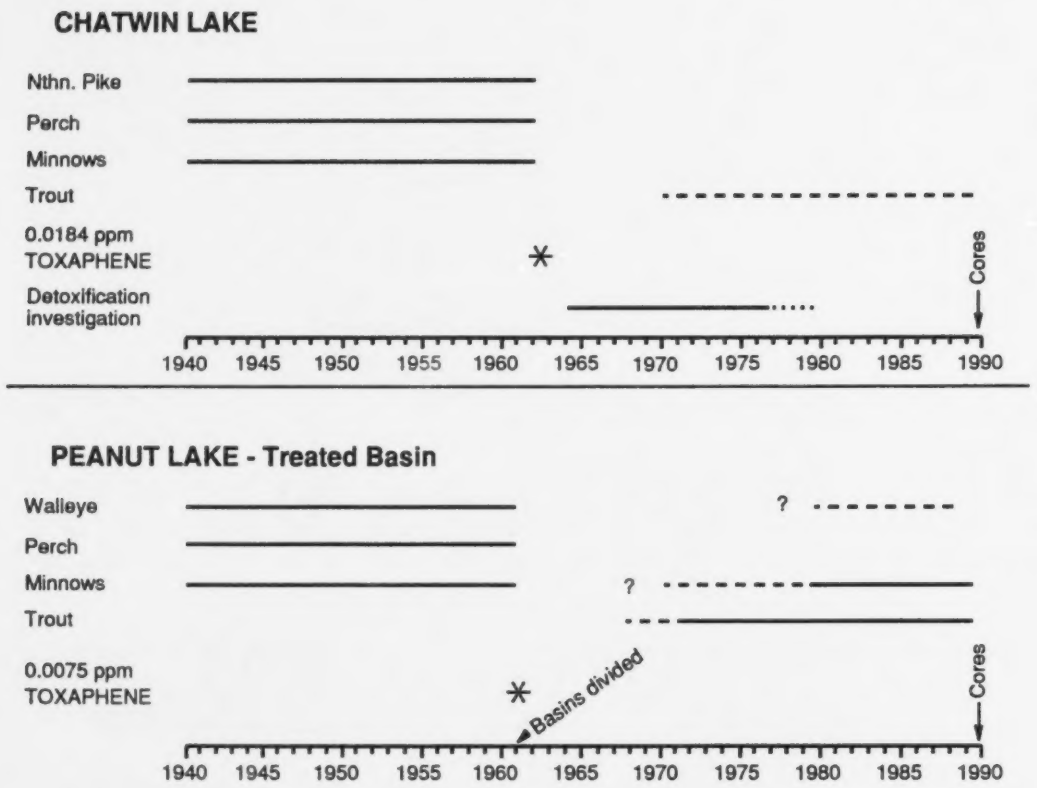

Figure II-1: Chronological history of known events in Chatwin Lake and Peanut Lake, Alberta, from 1940 to 1990.

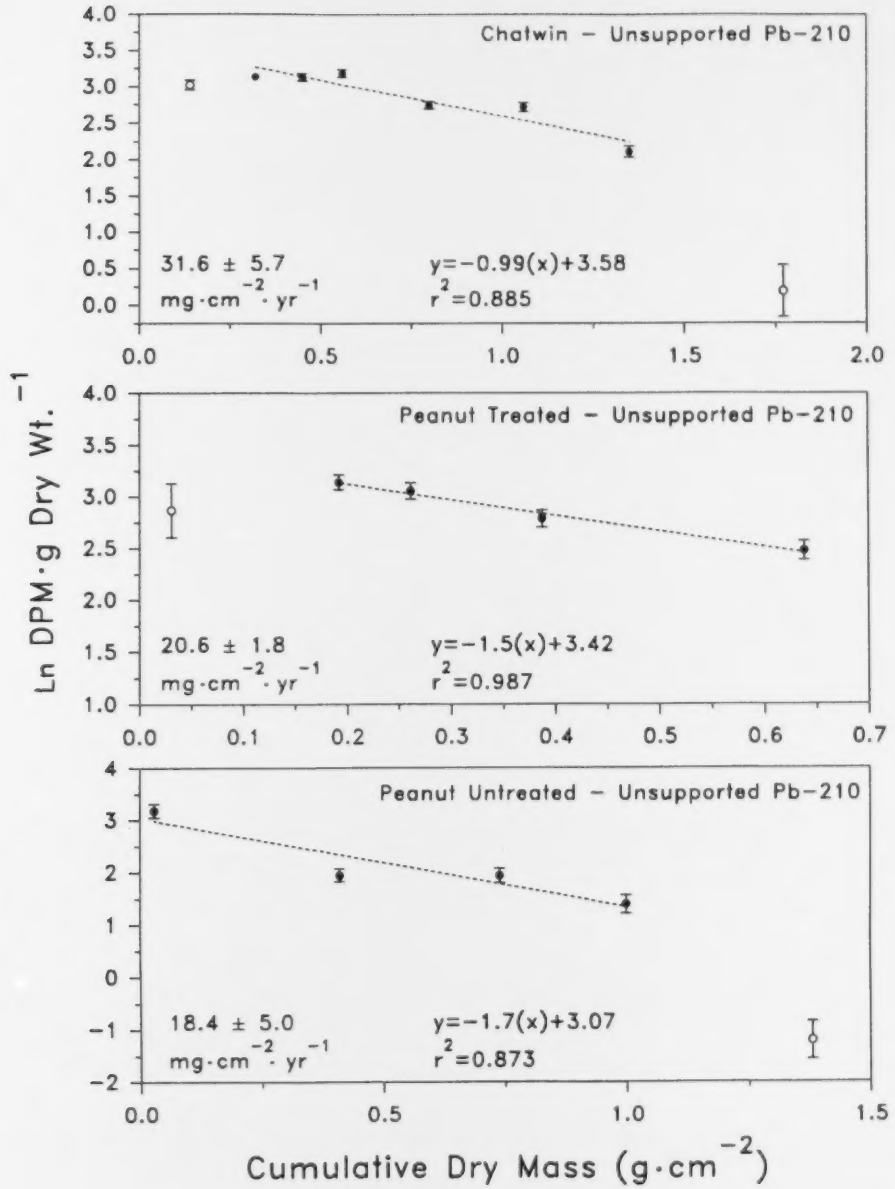

Figure II-2: Unsupported ^{210}Pb activity profiles from Chatwin Lake, and from the Treated and Untreated basins of Peanut Lake. Mean accumulation rates shown were derived from a ratio of the ^{210}Pb decay constant (-0.03112 yr^{-1}) and slope of lines. Empty points not included in equation because counts were too low or too close to background.

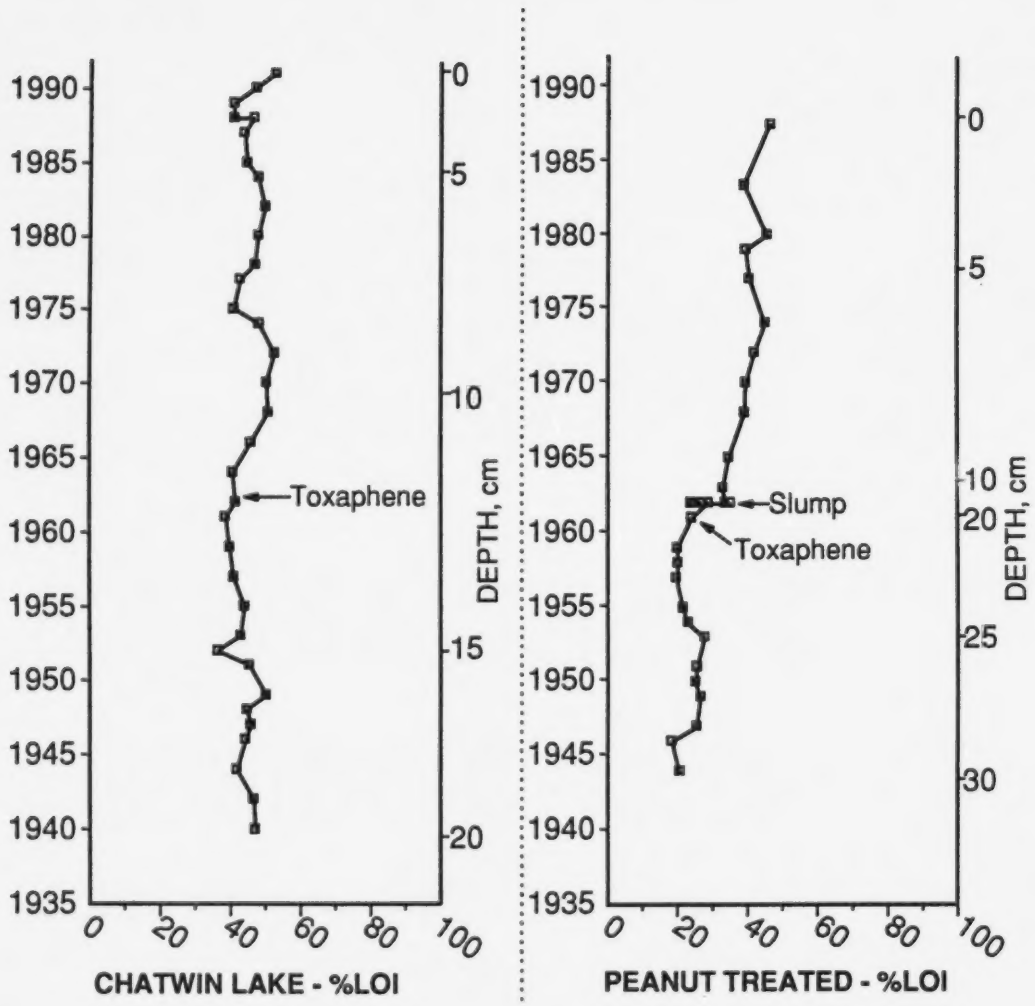

Figure II-3: Percent loss-on-ignition at ~0.5 cm intervals for the length of cores from each toxaphene-treated lake. Left axes show dates; right axes are depths corresponding to dates.

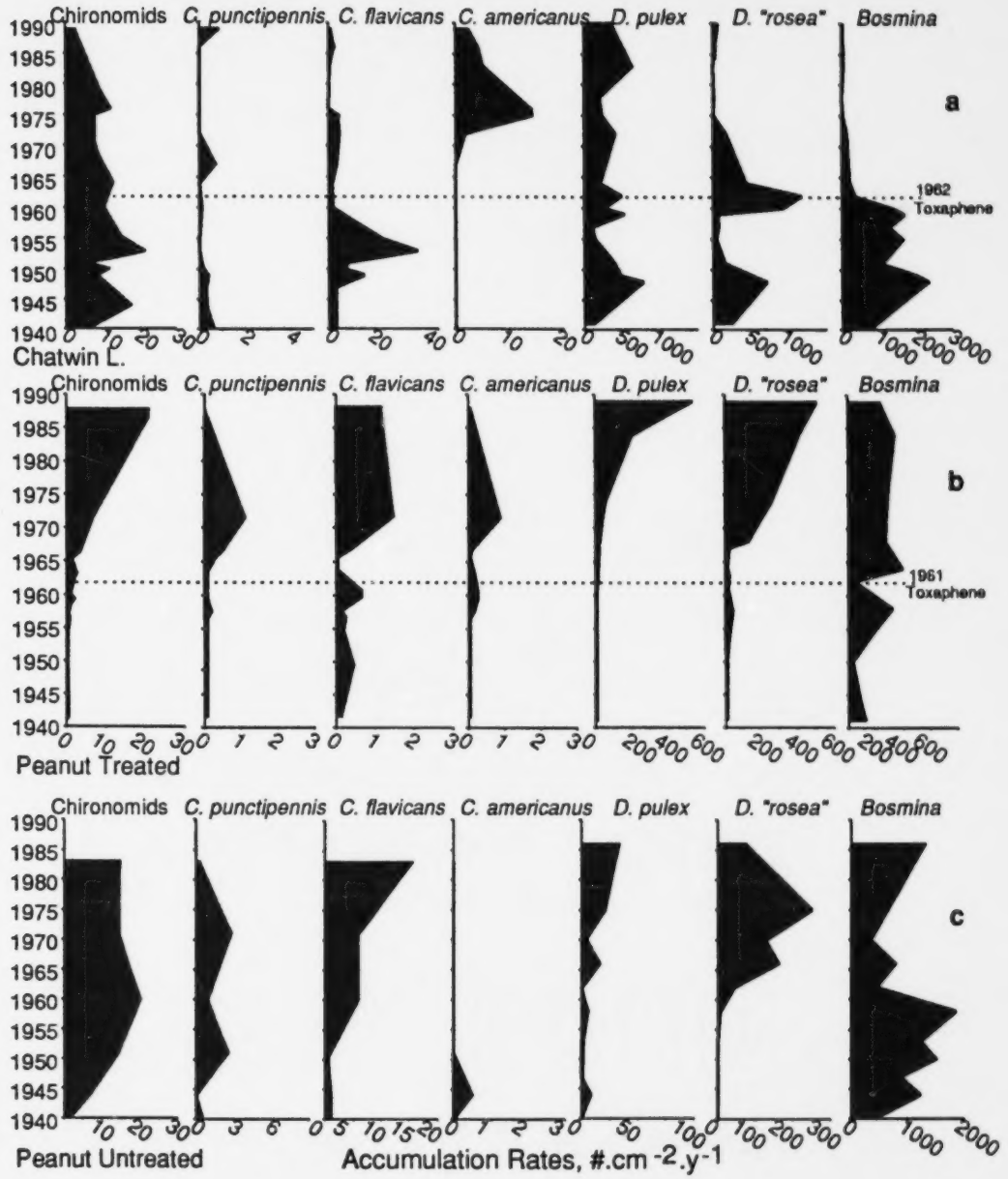

Figure II-4: Accumulation rates (#.cm^{-2}.yr^{-1}) of chironomids, *Chaoborus* spp., and planktonic cladocerans from sediment cores over 50 years. Chironomids = head capsules (total only), *Chaoborus* spp. = mandibles, *Daphnia* spp. = claw pairs ("*rosea*" in quotes due to similarity of claws to other types), *Bosmina* = headshields.
a) Chatwin Lake; **b)** Peanut Lake-Treated; **c)** Peanut Lake-Untreated.

III. PALEOLIMNOLOGICAL RECORD OF CLADOCERAN AND ALGAL RESPONSES TO FISHERY MANAGEMENT PRACTICES[4]

Introduction

Toxaphene was used as as an insecticide on agricultural crops and as a piscicide in lakes long before its wide-ranging toxicity and persistence were realized (Saleh 1991). Because it was seldom monitored, the effects of toxaphene on aquatic organisms other than fish is poorly known. Fortunately, historical changes in many aquatic populations may be partially reconstructed from the paleolimnological record. High resolution reconstructions of communities can provide important bridges between scattered field observations, as well as a better understanding of long-term lake dynamics (Frey 1976; Hann 1989; Leavitt et al. 1989).

Invertebrates in lakes have been known to respond negatively to the application of toxaphene (Cushing and Olive 1957; Stringer and McMynn 1958; Larkin et al. 1970; Hilsenhoff 1971; Webb 1980). Some organisms, such as many chironomids and oligochaetes, consistently recovered relatively quickly (Stringer and McMynn 1958; Webb 1980), whereas the abundance of others can be depressed for years (*Chaoborus* spp., Hilsenhoff 1971; Webb 1980). Further, planktonic cladocerans are frequently affected at moderate to high dosages (Hoffman and Olive 1961; Larkin et al. 1970).

Chydorids are microscopic (<0.5 mm) cladocerans that are abundant in the shallow waters of lakes, but their response to toxaphene treatment is unknown. On the other hand, chydorids are among the most diverse and distinctive animal taxa found in lake sediment cores, making them extremely practical for paleolimnological studies (Frey 1960; Frey 1976; Hann et al. 1994). Knowledge of environmental optima and tolerances of chydorids is less well known than for some other paleolimnological indicators (e.g. diatoms), but is expanding (Frey 1971; Goulden 1971; Whiteside et al. 1978; Hann 1981; Robertson 1990; Duigan 1992).

Toxaphene was used as an agricultural insecticide on croplands, therefore, it was not usually toxic to aquatic plants (reviewed by Bidleman et al. 1988; Saleh 1991). Toxaphene concentrations similar to those used in most lake treatments had no acute effect on algae in lab experiments (Schoettger and Olive 1961), although doses approximately 10-100 times higher (0.1-1.0 $mg.L^{-1}$), inhibited cell numbers in experiments with the green alga, *Scenedesmus quadricaudata* (Turpin) (Stadnyk et al. 1971).

The composition of algal communities in lakes may, nevertheless, be altered by the indirect effects of toxaphene poisoning. For example, loss of planktivorous fish can allow increased biomass of large-bodied herbivores which, in turn, may selectively feed on small algal species (Shapiro and Wright 1984; Carpenter et al. 1987; Leavitt et

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[4] A version of this chapter was submitted 1 September 1994 for publication in *Freshwater Biology*. Miskimmin, Schindler and Leavitt.

al. 1989). Increased water clarity often promotes deep bloom-forming algae (Pick et al. 1984) and increased macrophyte biomass (providing habitat for chydorids; Whiteside 1970). Sedimentary pigments may be used to reconstruct many such changes in aquatic plant communities (Sanger 1988; Leavitt et al. 1989).

Using paleolimnological techniques, I examined the response of Chydoridae and algal groups (based on pigment analysis) to toxaphene treatment and subsequent fish stocking in an oligotrophic montane lake and a eutrophic prairie lake. The former was treated in 1957, the latter in 1962. I also report remains of planktonic Cladocera and total Chironomidae in the oligotrophic lake to complement similar data already published for the eutrophic lake (Miskimmin and Schindler 1994). I compare changes between lakes and within lakes before and after treatment with toxaphene. My historical reconstructions based on sediment core data are compared with available contemporary information.

Materials and Methods

Study Sites

The two western Canadian lakes studied share a common history of toxaphene treatment and trout stocking, but are different in productivity and chemical characteristics (Table III-1). Annette Lake is an oligotrophic lake located in a montane coniferous forest region (*Pinus contorta* Loudon and *P. albicaulis* Engelm. dominated) of Jasper National Park, Canada, while Chatwin Lake is eutrophic and located in a boreal mixedwood region (*Populus tremuloides* Michx. dominated) of the Canadian prairies. The chemical and fisheries regimes of the lakes were occasionally monitored in the past: Parks Canada and Canadian Wildlife Service archived some information for Annette Lake (Anderson and Donald 1978), and Alberta Department of Fish and Wildlife monitored the basic chemistry of Chatwin Lake (Table III-1).

Annette Lake (alt. 1024 m) is typical of montane lakes in the Canadian Rocky Mountains. Water transparency during the open water season is high (>12 m secchi) and phosphorus concentrations are low (Table III-1). The littoral zone has sparse patches of *Chara* sp. and a few other macrophytes, but is mostly rocky or sandy. The drainage basin is unmodified by development or agriculture, aside from serving as a day-use area for tourists. The natural fish in the lake were longnose sucker (*Catostomus catostomus* (Forster)) and lake chub (*Couesius plumbeus* (Agassiz)). The lake has been stocked with various salmonids since the early 1900's, and was treated in 1957 with an unknown concentration of toxaphene to extirpate all fish (Anderson and Donald 1978). Following treatment, brook trout (*Salvelinus fontinalis* (Mitchill)) and rainbow trout (*Oncorhynchus mykiss* Walbaum) were stocked. Lake chub and longnose suckers apparently reinvaded and are presently the most abundant fish in the lake, although a few brook trout remain (Donald D.B., Environment Canada, pers. commun.). The diverse invertebrate community during the summer includes a variety of Ephemeroptera, Trichoptera, Gastropoda, and Amphipoda. Historical data indicate that numerous cladoceran species found in sediment cores from Annette Lake, were also found in survey samples taken in the 1920's and the 1970's (Table III-2).

Chatwin Lake is located in an agricultural area of the prairies approximately

500 km northeast of Annette Lake. Prior to toxaphene treatment in 1962, the fish community consisted of northern pike (*Esox lucius* Linnaeus), yellow perch (*Perca flavescens* (Mitchill)) and brook stickleback (*Culaea inconstans* (Kirtland); Alberta Dept. of Fish and Wildlife files). To briefly summarize the stocking history following the toxaphene treatment, rainbow trout were stocked since the mid-1960's with minimal success, and the lake now has only a sparse rainbow trout population (Hugh Norris, Alberta Dept. of Fish and Wildlife, pers. comm.). The littoral zone has extensive beds of emergent and submergent macrophytes during the summer season, and large-bodied invertebrates are abundant (notably *Gammarus lacustris* Sars, *Hyalella azteca* (Saussure), *Chaoborus* spp.).

Sediment Core Collection

Two sediment cores were collected by freeze-coring (O'Sullivan 1983) at the deepest site on each lake (Table III-1). Distinct laminations throughout the Chatwin Lake cores and a single 2.5 cm wide band at 6-8.5 cm in depth in Annette Lake cores, verified that sediments were relatively undisturbed by the coring process. The cores were immediately wrapped in aluminum foil, returned to the laboratory on dry ice, and stored at -10°C until further use. Cores were cut in lengthwise quarters with a band saw, and the exterior surfaces scraped clean with a woodplane to remove mixed surfaces.

Quarter sections of cores were analysed for cladoceran and chironomid remains, toxaphene residue, ^{210}Pb chronology, ^{137}Cs (Annette Lake only), plant pigments and organic matter. Non-chydorid invertebrate remains are only included here for Annette Lake to complement data for Chatwin Lake (Miskimmin and Schindler 1994). All analyses could not be done on individual quarter sections of a core because of the quantities required, so a total of four or five quarter sections for each basin were used to complete the study. Matching laminae and other distinctive markers were used to ensure depth correlation among sections.

Sediment Dating, Toxaphene and Organic Content

A combination of varve estimates (Chatwin Lake), physical markers, radiometric assays, and toxaphene analyses were used for dating sediments. Varves (annual sets of laminae) in Chatwin Lake were distinguished as regularly repeated colour bands that were counted independently by two individuals, and that corresponded with a 1962 toxaphene maximum at 11.5 cm (Miskimmin and Schindler 1994). The average varve width in the upper 12 cm of the core was ~0.35 cm. A single 2 to 3 cm wide band (not a varve) in Annette Lake sediments was useful for matching core depths only.

Pb-210 chronology was applied to sediments from both lakes by sampling 2-5 mL of sediments per sample (~1 cm in depth). Sediment deposition was calculated using the constant rate of supply model described by Eakins and Morrison (1978).

For Annette Lake sediments, in addition to ^{210}Pb dating, ^{137}Cs dating was performed on aliquots of freeze-dried sediment sampled approximately every 1 cm. The caesium dating procedure is based upon the known global maximum deposition of

^{137}Cs from in the early 1960's (Olsson 1986). Cs-137 was measured by direct gamma spectrometry (by Dr. M. Stephenson, Atomic Energy of Canada Ltd., Pinawa, MB), using a high purity germanium intrinsic p-type well detector (Princeton Gamma-Tech), linked to a Nuclear Data 6700 multichannel analyzer computer, scanning the 662 KeV photon peak. This ^{137}Cs procedure is non-destructive, permitting the same samples to be used for toxaphene analyses.

Toxaphene was determined on freeze-dried 0.8 to 1.0 cm slices of a core, identical to sampling methods described in Miskimmin and Schindler (1994) and analytical procedures in Muir et al. (1988). Briefly, freeze-dried samples were Soxhlet-extracted with dichloromethane (DCM), then separated from other chlorinated organics on a Florisil column. After elution with hexane:DCM (85:15), extracts were analysed by electron capture detector gas chromatography (Varian 6000). Results were verified by negative chemical ionization mass spectrometry in selected-ion mode. Because technical toxaphene is particle-reactive, the maximum toxaphene concentration was assumed to represent the approximate year of lake treatment.

Organic content, defined as percent loss-on-ignition (% LOI) of sediments after burning at 550°C for 1.5 h, was measured at 0.3 to 1 cm intervals in sediment cores from the two treated lakes.

Cladocera

Samples were taken at 0.5 to 1.0 cm intervals from a thawed core section. Following the general procedure of Frey (1986), 1 mL of sediments per interval was added to 15 mL of 10% KOH, gently heated, and occasionally swirled for 5 hours. Supernatant KOH was decanted and the sediments diluted at least three times with distilled water. For all Chatwin Lake samples, and for *Daphnia* and *Bosmina* remains in Annette Lake samples, counts were done without sieving; for Chydoridae, Annette Lake sediments were passed through a 93 µm sieve to remove excessive fine particles ("rock flour"). Some small chydorid remains may have been lost with sieving, however, the larger and more easily identifiable components (headshields and carapaces) were retained. The final volume was brought to 5 or 10 mL and subsampled to slides (50 µL per slide) using glycerin jelly stained with lignin pink as a mounting medium (Hann 1989). A Nikon phase contrast microscope was used to identify and enumerate cladoceran remains from four slides (200 µL), or until total remains exceeded 150 per sample.

Data are reported as a count of claws (*Daphnia*), headshields or carapaces (chydorids and *Bosmina*), representing remains.g^{-1} dry weight and relative percent (daphnids only) at a given sample depth. Identification of remains was based on Brooks (1959), Frey (1959, 1960), Dodson and Frey (1991) and Hann (1989), and by comparing remains with contemporary samples from the region, where possible. In some cases where abundances were low or specific identifications were not possible, chydorid species were numerically combined by genera. For Chydoridae, diversity indices (Shannon-Wiener, e^H and Simpson's, 1/D; Krebs 1989) and species richness (number of taxa per 1000 individuals) were calculated at each depth.

Chironomid Remains

Chironomid head capsules from Annette Lake cores were enumerated in 3 mL sediment core samples as described in Miskimmin and Schindler (1994). Briefly, sediments were deflocculated with 20-25 mL of 10% KOH, head capsules were concentrated onto a 93 µm mesh, and rinsed into a plankton counting tray. The mesh was checked for remains that adhered to it, but no attempts were made to quantify any earliest instar head capsules that might have passed through. Total chironomid head capsules were enumerated using a dissecting microscope. Results are reported as accumulation of head capsules per g (dry wt).

Plant Pigments

A frozen quarter core section was freeze-dried for 24 h, leaving a frozen base underlying about 4 mm of dried sediments. All sectioning was done at -10°C under dim indirect lighting. Samples were removed every 0.5 to 1.0 cm for the length of the core and placed in 20 mL glass vials. Before analysis, samples were re-lyophilized to remove residual moisture. Carotenoids, chlorophylls and their derivatives were extracted by soaking a 5 to 15 mg subsample of dry sediment in 5 mL of acetone:methanol:water (80:15:5 by vol) for 24 h at 10°C in the dark (Leavitt and Brown 1988). All other extraction steps are as described in Appendix B and Leavitt and Carpenter (1989). Pigments were quantified by reversed-phase HPLC as described by Leavitt et al. (1989) and are expressed as nmol pigment.g^{-1} dry weight of sediments. Cluster analysis that calculates a dissimilarity matrix based on Euclidian distances, identified relationships among pigment assemblages by depth (Rohlf 1987).

Statistical differences

Differences between group means for chydorid and pigment data were estimated using pooled estimates of variance. Means were compared between all samples both before and after toxaphene treatment (long-term), as well as three samples before and after treatment (short-term).

Results

Sediment Dating and Toxaphene

In Chatwin Lake, the toxaphene maximum of 1602 ng.g^{-1} occurred at 11.5 cm depth (Fig. III-1), or 1962 as estimated by ^{210}Pb assay and by varve counting (Miskimmin and Schindler 1994).

In Annette Lake, ^{210}Pb estimated sediment accumulation rates were much lower than was possible based upon the two other dating procedures, ^{137}Cs and the toxaphene maximum, that specifically indicated the early 1960's and late 1950's. Since littoral slumping may have occurred, ^{210}Pb values and detailed dates were not used for Annette Lake. ^{137}Cs activities peaked at 6.5-7.5 cm, coincident with the sediment sample with the highest toxaphene concentration (240 ng.g^{-1}), dating this sample to the early 1960's (Fig. III-2). Toxaphene was more extensively distributed in Annette Lake sediments with depth than Chatwin Lake sediments, although the concentrations were much higher in Chatwin Lake sediments (Figs. III-1 and III-2).

Organic Content

The sediment organic content as estimated by %LOI was twice as high in eutrophic Chatwin Lake as in oligotrophic Annette Lake (Figs. III-1 and III-2). In Chatwin Lake, there was a temporary increase in %LOI following toxaphene treatment, although the proportions were only slightly higher than maxima in the distant past (Fig. III-1).

In Annette Lake, %LOI increased coincident with toxaphene and ^{137}Cs maxima, reaching higher proportions than had ever occurred deeper in sediments (Fig. III-2). Percent LOI remained at the higher proportion between about 6 to 8 cm, then in shallower sediments, returned to proportions similar to those found in deeper sediments. The higher %LOI at 6 to 8 cm was observed as the dark band in sediment cores from Annette Lake.

Chydoridae

Most chydorid taxa in Chatwin Lake (Fig. III-1), and many in Annette Lake (Fig. III-2), were generally less abundant in recent sediments (post-toxaphene) than in deeper sediments deposited prior to the toxaphene treatments and trout stocking.

Specifically, in Chatwin Lake, either *C. cf. sphaericus* or *Alona* spp. were numerically dominant before and after treatment. Chydorids in Chatwin Lake were historically most abundant during the 1940's and 1950's (pre-toxaphene). Around the time of toxaphene treatment, mean abundances differed among taxa (comparing three depths before and three depths after treatment), with no significant change in *Leydigia leydigi* and *Pleuroxus* spp. ($P \geq 0.05$), and decreases in *Chydorus cf. sphaericus*, *Alona* spp. and *Camptocercus* sp., ($P \leq 0.05$; Fig. III-1). *Acroperus harpae*, *Alona* spp. and *Eurycercus* sp. never reached their former pre-toxaphene high abundances in the entire period following toxaphene treatment.

In Annette Lake, taxa that were more abundant in combined pre-toxaphene years compared to post-toxaphene years included *C. cf. sphaericus*, *C. gibbus*, *Eurycercus* sp., *Alona affinis*, *A. quadrangularis*, and *Alonella nana* ($P \leq 0.05$). Many chydorids appeared to decline near the year of treatment (1957), although in most cases, the decline commenced prior to this date (Fig. III-2). *A. excisa*, small *Alona* spp. and *Acroperus harpae* were not significantly changed by the toxaphene treatment ($P \geq 0.1$; Fig. III-2).

Chydorid diversity was similar before and after toxaphene treatment in both treated lakes (Table III-3). No differences in diversity between the two lakes existed for all depths combined, all pre-treatment samples or for all post-treatment samples (Table III-3). In Chatwin Lake, mean species richness (number of taxa per 1000 remains) was higher in all samples grouped after toxaphene treatment compared to before treatment ($P \leq 0.01$), but there was no such difference for Annette Lake ($P \geq 0.05$). Conversely, the number of taxa per sample was higher before treatment compared to after treatment in Annette Lake ($P \geq 0.05$), but not in Chatwin Lake. The overall chydorid species richness found in sediment core samples was significantly higher in oligotrophic Annette Lake than in eutrophic Chatwin Lake (Table III-3).

Other Cladocera and chironomids (Annette Lake only)

With only one exception, maximum accumulations of *Daphnia* spp., *Bosmina* sp. and total Chironomidae corresponded with the samples with higher %LOI described above (Fig. III-3). The exception of decreased accumulation of *D. rosea* in one sample occurred at ~7.5 cm, near the depth of the maximum toxaphene concentration. A switch in *Daphnia* dominance, representing a change from a smaller-bodied (*D. rosea*) to a larger-bodied daphnid (*D. pulex*), occurred from pre-treatment to post-treatment years (Fig. III-3). The dominance of *D. pulex* has persisted as evidenced by both near interface core samples (Fig. III-3) and plankton samples taken in 1992 (data not shown), where large-bodied *D. pulex* were the most abundant daphnid in Annette Lake.

Plant pigments

The overall plant pigment concentrations were often up to 10 times higher in eutrophic Chatwin Lake sediments than in Annette Lake sediments. In Chatwin Lake, pheophorbide *a* and alloxanthin levels increased for about 25 years following toxaphene treatment, but on average, most other pigments were unchanged throughout the cores (Fig. III-4).

In Annette Lake, alloxanthin, pheophorbide *a*, chlorophyll *a*, lutein-zeaxanthin, beta-carotene, pheophytin *a* and fucoxanthin, all increased in mean concentration in the years after toxaphene treatment ($P \leq 0.05$; Fig. III-5). Conversely, diatoxanthin, chlorophyll *b* and an unidentified pigment that eluted closely following chlorophyll *c* early in the UV-visible spectra (labelled "green-x"), decreased following toxaphene treatment ($P \leq 0.005$). The pigment increases occurred about the same time as toxaphene treatment, although most of the pigment decreases occurred several years later (Fig. III-5).

In Annette Lake, cluster analysis revealed two distinct algal assemblages from before and after toxaphene treatment (all clusters shown; Fig. III-5). The pre-treatment assemblage was comprised of dinoflagellates, diatoms, *Euglena*, and chlorophytes. The post-treatment assemblage comprised cryptophytes, Cyanobacteria, diatoms, chrysophytes and chlorophytes (Fig. III-5). Less definite groups emerged in Chatwin Lake. Many post-treatment depths were closely related to pre-treatment depths, i.e. the algal assemblages were indistinct (all clusters not shown; Fig. III-4).

Discussion

In the absence of detailed sampling before, during and following toxaphene treatment that would provide the most accurate response of organisms in lakes, paleolimnology was the only way of reconstructing the effects of perturbation in these lakes. I acknowledge that paleolimnological techniques quantify only those organisms that preserve in sediments, and any "cause and effect" argument is dependent upon the established sediment chronology and knowledge of multiple interactions in the ecosystem. However, paleolimnology does permit the reconstruction of information that would otherwise be lost and provide an important long-term perspective to lake dynamics (Frey 1976; Hann 1989; Leavitt et al. 1989).

The fishery management practices of toxaphene application and trout stocking were associated with shifts in chydorid abundances, but not species diversity, in two Canadian lakes. Some decreases in abundance following toxaphene treatment persisted for the entire post-treatment period (e.g. *Chydorus* spp. or *Alonella* spp.). However, the absence of some rarer taxa in some post-treatment samples could not be attributed to the manipulations because they were also frequently found in low numbers or were absent in pre-treatment samples (Figs. III-1 and III-2).

My results are consistent with previous observations that chydorids exhibit a variable response to strong perturbations. In a similar paleolimnological study, Hann et al. (1994) noted that chydorid accumulation rates, species diversity and richness were similar before and after an experimental 10-fold increase in nutrient inputs to Lake 227 in Ontario. As in my study, they found no evidence for species extirpation following perturbation. In contrast, Tsukada (1972), found that a deposition of volcanic ash caused a severe disturbance to chydorids, including permanent extirpation of *Eurycercus*, a numerically abundant taxon. Similarly, Whiteside and Harmsworth (1967) found a decrease in chydorid diversity with increased algal production (using surface sediment remains).

The finding that overall chydorid diversity (e^H) was similar for both lakes despite extreme differences in trophic status of these lakes may be related to differences in available chydorid habitat in the two lakes. Mixed beds of macrophytes cover approximately 99% of the near shore zone of Chatwin Lake, but are sparse in Annette Lake. Whiteside and Harmsworth (1967) concluded that the presence and distribution of macrophytes was the primary factor determining chydorid diversity. Similarly, Hann and Warner (1987) found a significant positive relationship between the presence of macrophytes and chydorid abundance. Presumably, the lack of macrophytes in Annette Lake both currently and in historical reports (Anderson and Donald 1978) restricted microhabitat availability.

Chydorids that were abundant, molting or reproducing at the time of toxaphene application may have been negatively affected compared to those in resting stages. Chatwin Lake was treated in October 1962, a time of year when populations of adult chydorids can be high (Goulden 1971) and when resting eggs are produced (Frey 1987). Lower toxaphene concentrations (0.1 to 1.0 $\mu g.L^{-1}$) than used in toxaphene-treated lakes reduced the production of young in *Daphnia magna*, with the no-effect level of 0.07 $\mu g.L^{-1}$ (Sanders 1980) being much lower than the dose applied to Chatwin Lake (18.4 $\mu g.L^{-1}$). Sub-lethal concentrations of the pesticide Lindane, depressed the movement of filtering limbs of 2nd to 8th instar *D. pulex* by 25%, with newly molted animals being the most sensitive (Gliwicz and Sieniawska 1986). Among other organic chemicals, metavanadate apparently promoted the production of daphnid ephippial eggs, while 3,4-dichloroaniline depressed daphnid reproduction (van der Hoeven 1990). The effect of toxaphene on cladoceran ephippia production or viability has never been examined, although the protective value of cladoceran ephippial eggs in harsh natural conditions is well known (Goulden 1971; Frey 1987; De Stasio 1990; Duigan 1992).

Indirect impacts of toxaphene application may also have contributed to long-

term reductions in chydorid abundance. Elimination of small zooplanktivorous fishes often leads to increased abundance of invertebrate predators and increased mortality of small prey (Carpenter et al. 1987). Summer populations of chydorids are known to be depleted by invertebrate predation (Goulden 1971; Keen 1973; de Bernardi et al. 1987) or a combination of fish and invertebrate predation (Williams 1983). Large invertebrate predators including *Chaoborus* spp. became most abundant several years after treatment of Chatwin Lake, probably because of the poor survival of stocked trout and the absence of other fish (Miskimmin and Schindler 1994). These predators likely contributed to the elimination of small *Bosmina* (Miskimmin and Schindler 1994), and presumably had similar effects on other small Cladocera. Invertebrate predators, including some chironomids (Fig. III-3), may have been less important in oligotrophic Annette Lake than in Chatwin Lake, because of successful trout stocking and reinvasion of the lake by native fish (lake chub and longnose suckers; Anderson and Donald 1978).

The lake manipulation appears to have caused a long-lasting change of the algal assemblage and pigment preservation characteristics in the oligotrophic Annette Lake but not in eutrophic Chatwin Lake (Figs. III-4, III-5). In Annette Lake, chlorophytes and diatoms were replaced as dominants by chrysophytes, cryptophytes and Cyanobacteria shortly after toxaphene treatment. Cryptophytes, chrysophytes and Cyanobacteria are known to form stratified deep water or benthic populations following rapid increases in water clarity during food web manipulations (Leavitt et al. 1989). The presence of high concentrations of undegraded labile pigments (Chl *a*, fucoxanthin) in Annette Lake sediments following toxaphene application is consistent with increased abundance of deep water or benthic algae. Algae living closer to cold or anoxic hypolimnetic waters are more quickly removed from light, oxygen and high temperatures, and their pigments are selectively preserved (reviewed by Leavitt 1993). In contrast, labile carotenoids and chlorophylls from epilimnetic algae are rapidly degraded during gradual sinking (Leavitt and Carpenter 1990; Hurley and Armstrong 1991). The finding that labile indicators of total algal biomass (e.g. Chl *a*) increased following treatment, while stable indicators (β-carotene, pheophytin *a*) did not, supports the hypothesis that pigment preservation, rather than algal production, increased following toxaphene application in the oligotrophic lake. Despite the apparent return of native fish and only minor long-term effects on invertebrates, the algal community of Annette Lake did not revert to its historical composition in the 35 years following treatment (Fig. III-5).

Further support for improved pigment preservation following toxaphene treatment is the increase in pheophorbide *a* coincident with the increased abundance of large herbivores (Fig. III-3; Miskimmin and Schindler 1994). Toxaphene treatment preceded the replacement of small-bodied *Daphnia rosea* and *Bosmina* by larger *D. pulex* in both lakes (Fig. III-3; Miskimmin and Schindler 1994). This shift towards large, effective grazers of phytoplankton is expected to favour the preservation of pigments both because algal pigments bypass water-column degradation within rapidly sinking feces (Carpenter et al. 1988; Leavitt and Carpenter 1990), and because effective herbivory helps maintain high water clarity, and deep water or benthic algal

populations (Leavitt et al. 1989). In both lakes, the switch to dominance of *D. pulex* was accompanied by an increase in 'fossil' pheophorbide *a*, a derivative of Chl *a* produced during gut passage (Daley 1973).

Nutrients released from decomposing fish killed by toxaphene may have contributed to the observed short-term increases in algal biomass and organic matter deposition. In some lakes, increased organic matter following fish kills stimulates the production of macrophytes, oligochaetes (Cushing and Olive 1957) and rotifers (Hoffman and Olive 1961). As well, others have noted that fertilization from fish decay can lead to an increase in zooplankton production and water clarity (Hemphill 1954). Despite these disturbances, there were few long-term changes in the plant community of eutrophic Chatwin Lake resulting from lake manipulation.

Although pigment analyses indicate a shift in the algal community in Annette Lake, some pigments were apparently not affected strongly by the toxaphene treatment, changes in fish and invertebrate populations, or the preservation complexities discussed above. Diatoxanthin (found in diatoms and dinoflagellates) was unchanged throughout the period surrounding toxaphene treatment in Annette Lake cores (~6-9 cm depth; Fig. III-5). The stability of diatom and flagellate populations in Annette Lake is further corroborated by similarities in the historical records of Bajkov in the 1920's and Anderson and Donald in the 1970's. These findings are consistent with laboratory studies that report diatoms and flagellates were unaffected by 10 to 100 $\mu g.L^{-1}$ toxaphene treatments (Stringer and McMynn 1958).

Summary

Despite differences in trophic status, these lakes responded similarly in some ways to fishery management practices. Overall, the Chydoridae were resistant despite a perturbation that some other invertebrates and fish. Large-bodied planktonic cladocerans became dominant following toxaphene treatment in both lakes. As in the mesotrophic and eutrophic lakes discussed in Chapter II, no effects on total chironomids in the oligotrophic lake were detected. Pigment preservation may have been enhanced indirectly following treatment by the change to more effective herbivory that results in rapid deposition of pigments with feces. On the other hand, the composition of the algal community was significantly different following toxaphene treatment only in the lower productivity lake. The fact that toxaphene remains in these lake ecosystems over 30 years after treatment (Figs. III-1, III-2) is evidence of its long-term persistence and potential for food web contamination (see Chapter IV).

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Table III-1. Characteristics of study lake surface waters during the ice-free season. Chemistry samples for Chatwin Lake were collected in July 91 and June 92, and for Annette Lake in July 92.

	Chatwin Lake	Annette Lake
Year treated	1962	1957
Coring date	Feb 1991	Apr 1992
Latitude	54°15'N	52°54'N
Longitude	110°51'W	118°04'W
Area	71 ha	28.6 ha
Zmax	15.8 m	23 m
pH	9.2	8.3
Conductivity	1400 $\mu S.cm^{-1}$	300 $\mu S.cm^{-1}$
Alkalinity	16.4 $meq.L^{-1}$	2.5 $meq.L^{-1}$
TP	47 $\mu g.L^{-1}$	4 $\mu g.L^{-1}$
TDP	37 $\mu g.L^{-1}$	3 $\mu g.L^{-1}$

Table III-2. List of organisms found in Annette Lake during historical surveys before (1925-1926) and after (1970-1977) toxaphene treatment that were also found in my core samples. Methods used in historical surveys were not identical and may not have identified all organisms in the lake. Sources of data: [a] Bajkov (1929) and [b] Anderson and Donald (1978).

Before treatment[a]	After treatment[b]
Acroperus harpae (Baird)	*Acroperus harpae*
Alona quadrangularis (Müller)	*Bosmina longirostris*
Alonella nana (Baird)	*Chydorus sphaericus*[c]
Bosmina longirostris (Müller)	*Daphnia pulex*[f]
Chydorus sphaericus (Müller)[c]	*Daphnia rosea* Sars[d]
Daphnia longispina (Müller)[d,e]	*Leptodora kindti*[g]
Daphnia pulex Leydig	
Graptoleberis testudinaria (Fischer)	
Leptodora kindti (Focke)[g]	

[c] Now considered a "species complex" (Dodson and Frey 1991).

[d] *Daphnia longispina* and *D. rosea* were probably the same species (Pennak 1978); indistinguishable based on remains of claws in cores.

[e] Most abundant daphniid in Bajkov's samples.

[f] Most abundant daphniid in Anderson and Donald's samples.

[g] One caudal spine only found in my sediment core samples.

Table III-3. Diversity and species richness of chydorids in Annette Lake and Chatwin Lake sediment cores. All values are Mean ± 1SD.

	Annette L.	**Chatwin L.**
All depths combined:	(n=15)	(n=21)
Shannon-Wiener (e^H)[5]	2.63±0.87	3.01±0.40
Simpson's (1/D)	1.74±0.53	2.41±0.38
Species Richness, #/1000	4.31±2.87	0.59±0.56
and # in sample	8.20±1.70	5.4±1.50
Pre-treatment:	(n=5)	(n=14)
Shannon-Wiener (e^H)	2.81±1.20	2.94±0.42
Simpson's (1/D)	1.90±0.77	2.31±0.38*
Species Richness, #/1000	3.65±4.21	0.35±0.18**
and # in sample	9.80±1.60**	5.80±1.40
Post-treatment:	(n=10)	(n=7)
Shannon-Wiener (e^H)	2.54±0.54	3.13±0.33
Simpson's (1/D)	1.66±0.26	2.62±0.29*
Species Richness, #/1000	4.64±2.14	1.07±0.77**
and # in sample	7.40±1.00**	4.70±1.30

* Post-treatment significantly higher than Pre-treatment ($P<0.05$).

** Significant difference between Pre- & Post-treatment ($P<0.01$).

[5] Number of equally common species to produce the observed species richness. The closer the value to the actual no. of species the more evenly distributed the species are.

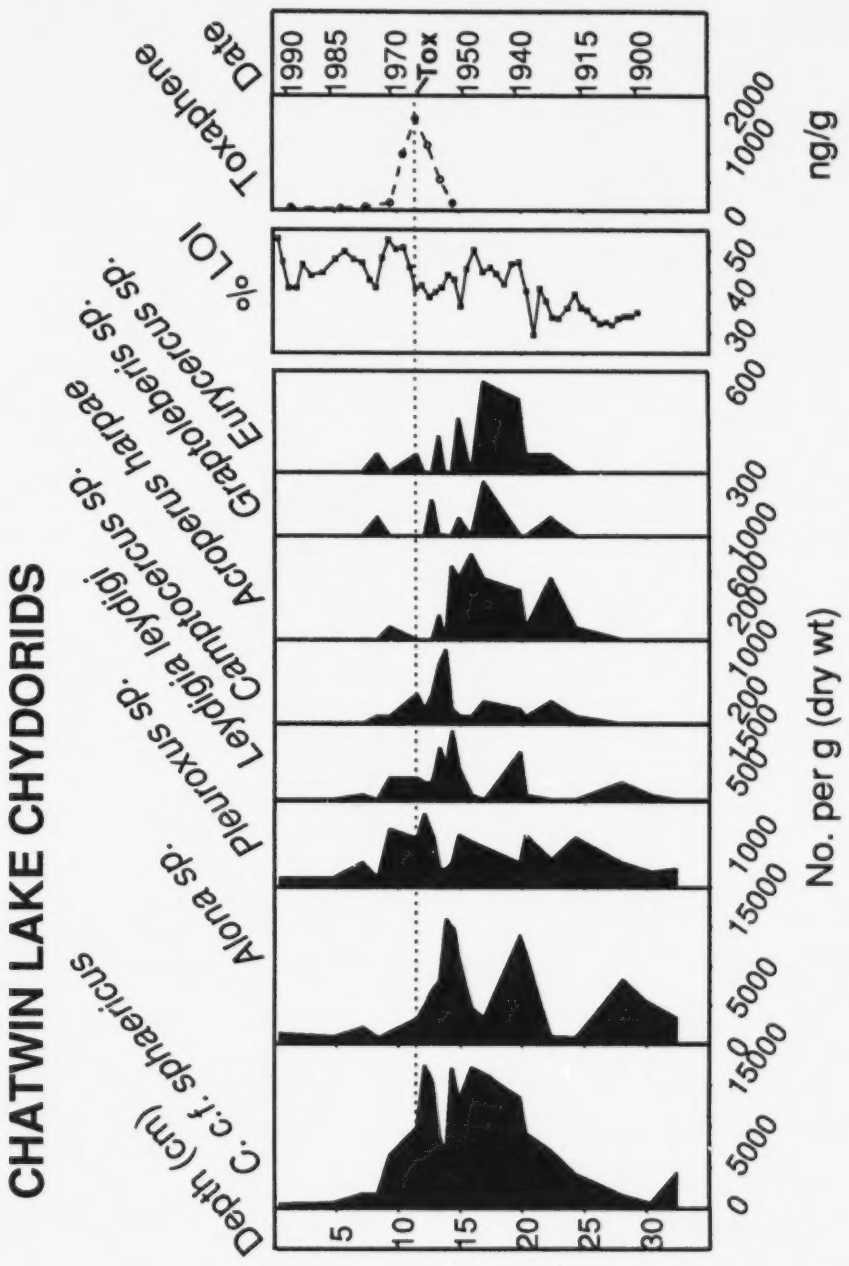

Figure III-1: Chatwin Lake - Chydorids, percent loss-on-ignition (%LOI) and toxaphene in sediment core samples representing approximately the last century. Chydorids were enumerated by counting headshields or carapaces.

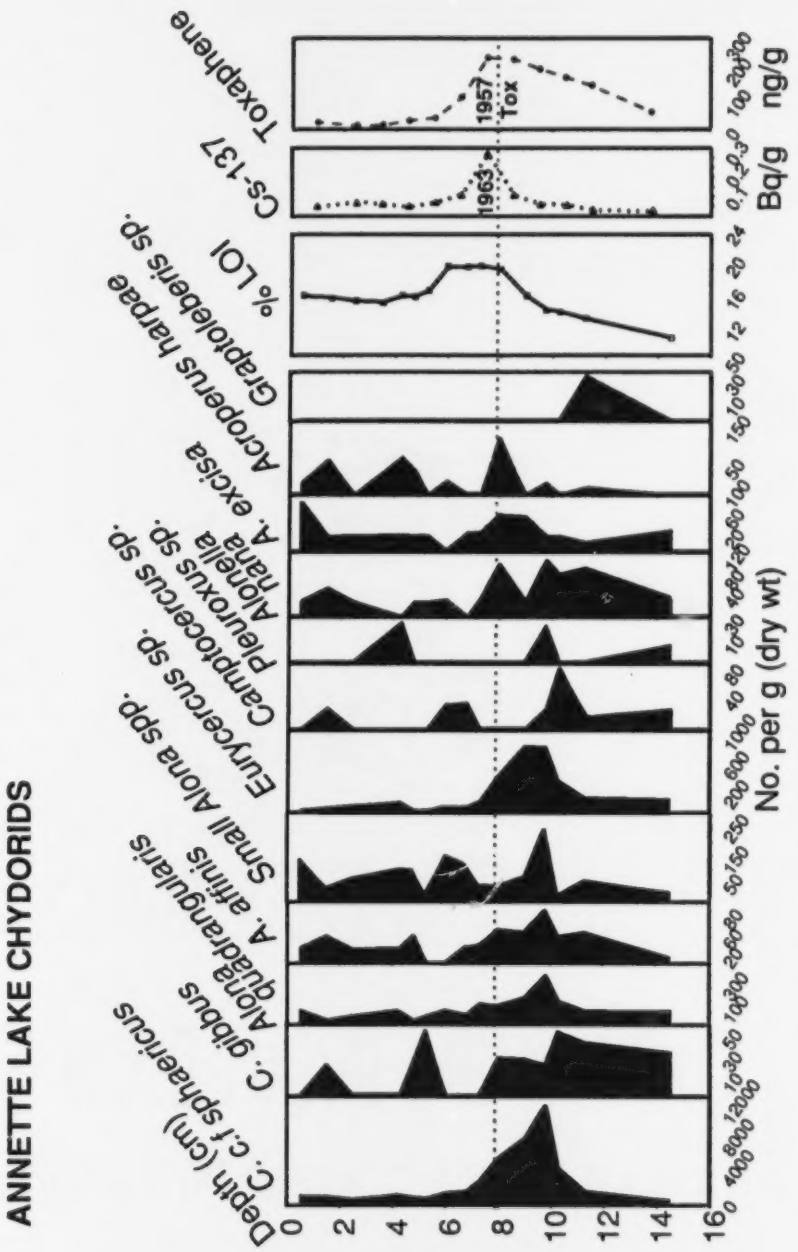

Figure III-2: Annette Lake - Chydorids, %LOI, ^{137}Cs, and toxaphene in sediment core samples with specific dates as shown.

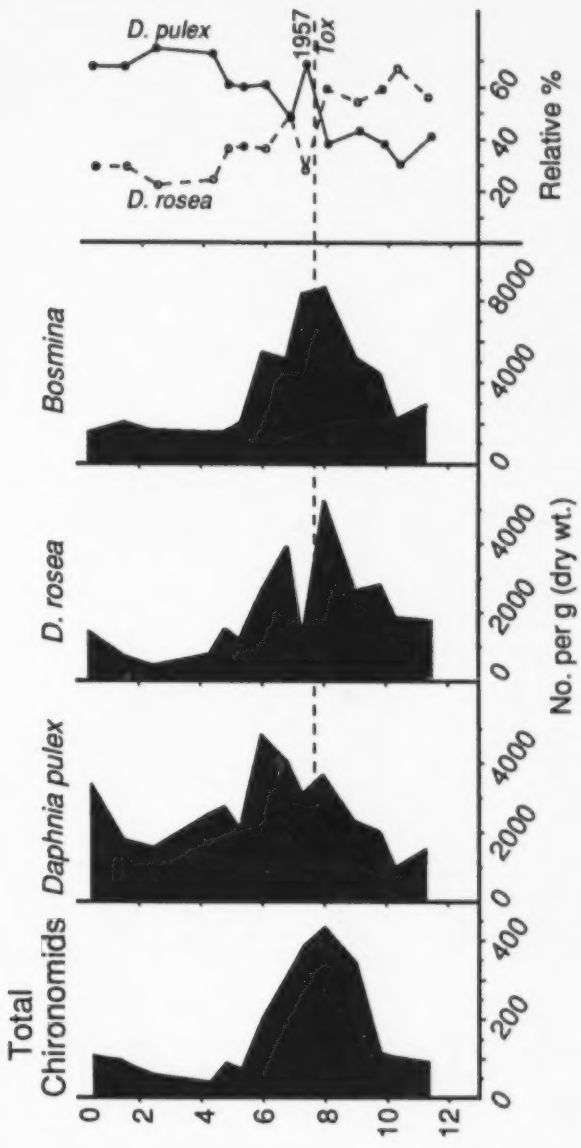

Figure III-3: Annette Lake - Total Chironomidae and planktonic Cladocera remains in sediment core samples. Relative abundance of the small (*D. rosea*) and large (*D. pulex*) daphnids illustrate dominance change over time.

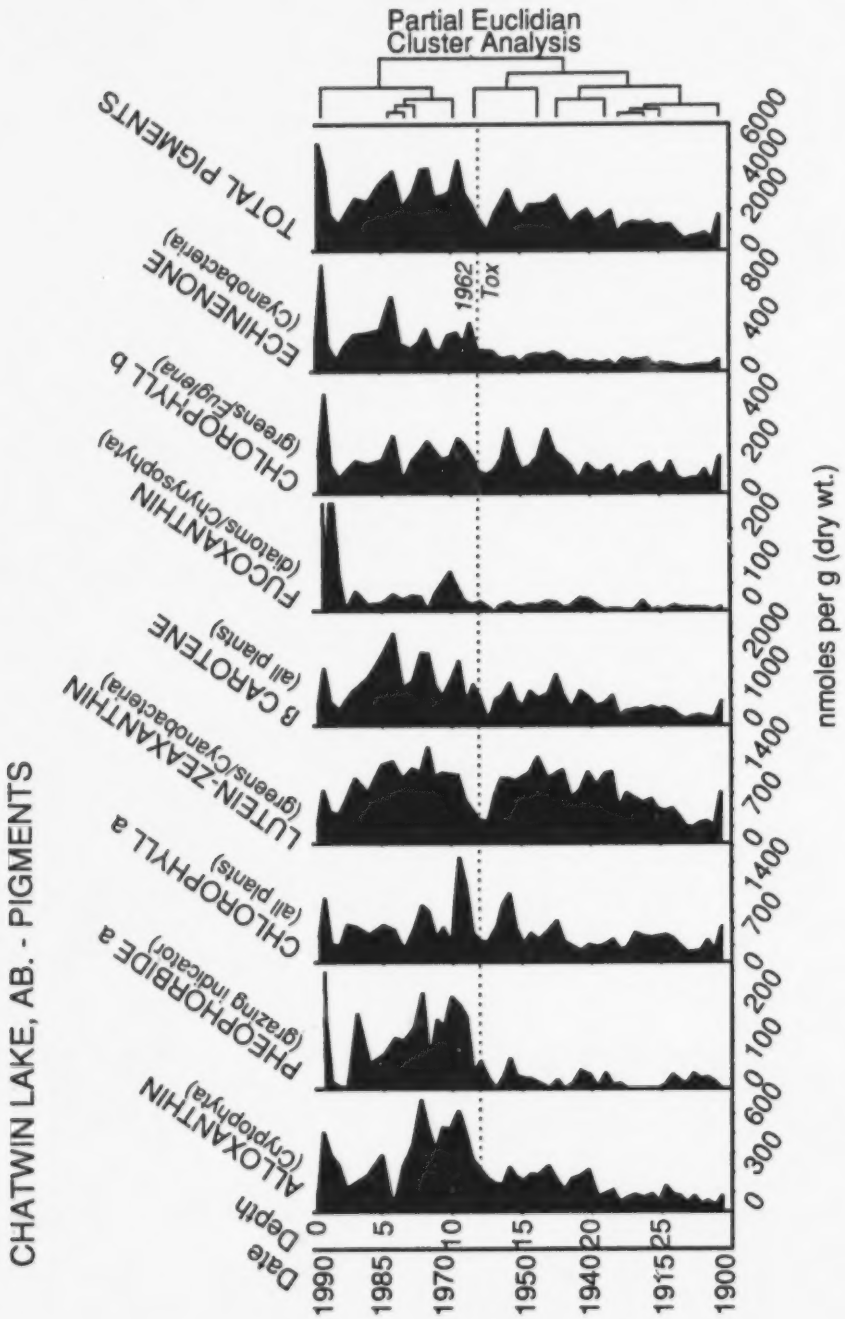

Figure III-4: Chatwin Lake - Plant pigments in core samples as determined by RP-HPLC analyses. Cluster analysis is based on Euclidian dissimilarity indices.

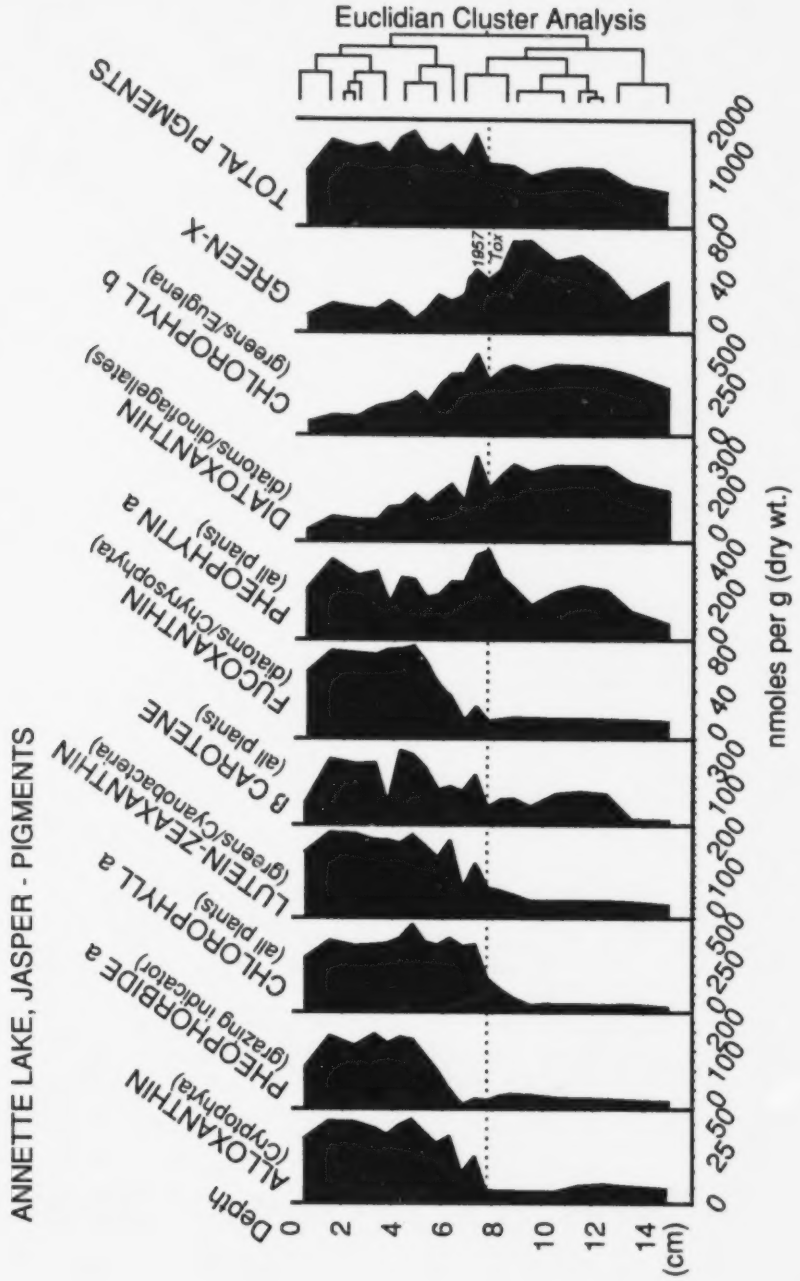

Figure III-5: Annette Lake - Plant pigments in core samples as determined by RP-HPLC analyses. Cluster analysis is based on Euclidian dissimilarity indices.

IV. CHLOROBORNANES IN SEDIMENTS AND FISH THIRTY YEARS AFTER TOXAPHENE TREATMENT OF LAKES[6]

Introduction

Toxaphene is an organochlorine insecticide (also called camphechlor) that was once widely used as a pesticide and briefly used as a fish toxicant during the late 1950's and 1960's in many North American lakes. It is composed of hepta- to decachloro- camphene derivatives, mostly chlorinated bornanes (CHBs). Analysis of sample for toxaphene by resolution gas chromatography can show more than 200 compounds (Saleh 1991; Vetter 1993).

While others have studied the residues of toxaphene in disposal sites or croplands where it was primarily used, relatively little is known about the long-term fate of toxaphene in aquatic environments where it was directly applied. For example, toxaphene is known to leach through sandy soils (Jaquess et al. 1989), topsoil (LaFleur et al. 1973) and anaerobic saline marsh soils and plants (Gallagher et al. 1979), but similar data on distribution and movement in lake sediments are lacking. Other aspects such as short-term degradation (Lee et al. 1977; Williams and Bidleman 1978), the role of lake sediments in complexation of toxaphene (Veith and Lee 1971), and the fate of various toxaphene fractions in model freshwater ecosystems (Isensee et al. 1979) have been examined.

Reductive dechlorination or dehydrochlorination are considered the main pathways resulting in losses of the higher chlorinated forms of toxaphene (Saleh and Casida 1978), however, complete degradation of the compound does not usually result. The more water soluble components are apparently formed relatively quickly after introduction of the parent compound to sediments (a few days: Williams and Bidleman 1978; 3 weeks: Harder et al. 1983; several months: Hughes and Lee 1973). No previous studies have addressed the long-term (decades) distribution in sediments and congener-specific characteristics of residual toxaphene from lakes that were directly treated with the chemical.

Recent studies using high resolution gas chromatography and electron capture negative ion mass spectrometry (GC-ECNIMS) have demonstrated the persistence of some CHB congeners in biota (Bidleman et al. 1993; Stern et al. 1992) and in air samples (Barrie et al. 1993). In both biotic and abiotic samples, the pattern of CHB peaks is dominated by a limited number of hepta-, octa- and nonachlorobornanes indicating the majority of the components in the original toxaphene mixture have been dechlorinated (Muir and de Boer 1993). Detailed GC-ECNIMS peak patterns of CHBs in sediments have not been previously reported.

Because of the demonstrated persistence of these and other congeners of toxaphene, as well as reports of elevated toxaphene in regions remote from direct application (Muir et al. 1990; Bidleman et al. 1989; McConnell et al. 1993), I believed

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that lakes that were previously treated with the compound should be examined for toxaphene residues. The objectives of this study were to examine the distribution of toxaphene in profundal START HERE sediment cores from two treated and one untreated lake, and to compare chromatographic patterns between recent and older sediments and fish from the two treated lakes. The known additions of toxaphene during the early 1960's permitted the evaluation of persistent organochlorine compounds as sedimentary date markers (critical to paleoecologists), and the assessment of current analytical methodology for CHBs in environmental samples.

Materials and Methods

Sediment collection and preparation

Sediment cores were collected by using a freeze corer (Shapiro 1958; O'Sullivan 1983) at the deepest site of three Alberta lakes: two were treated with toxaphene in 1961-1962, and one was untreated. This coring process has the advantages of collecting undisturbed sediments (evidenced by preserved laminations), and freezing the sediments immediately upon collection to prevent chemical losses.

Peanut Lake (54°01'N, 114°21'W; mesotrophic) was treated with 7.5 $\mu g.L^{-1}$ of toxaphene in September 1961, and Chatwin Lake (54°15'N, 110°51'W; eutrophic) was treated at 18.4 $\mu g.L^{-1}$ in October 1962. In Peanut Lake, an 11.5 cm unlaminated interval (referred to as a "slump"), occurred between 9.5 - 21 cm, resulting in the deep location in sediments of the toxaphene maximum. The untreated lake, Peanut Lake Untreated, is a distinct basin of Peanut Lake that was separated by a berm at the time of treatment to prevent native fish from reinvading the treated basin in years of high water. The upper 5 cm of sediments from the untreated basin were analysed for toxaphene, representing a control. Other characteristics of Peanut and Chatwin Lakes are given in Miskimmin and Schindler (1994).

Frozen cores, about 30 cm in length, were sliced lengthwise in quarters with a band saw, then either freeze-dried completely before sectioning or sectioned with the saw prior to freeze-drying. Sections usually represented 1 or 2 cm slices in sediments, except surface sediments that represented 3-5 cm to provide the sample size necessary for toxaphene analysis. Nine samples from each core provided a toxaphene profile for each of the two treated lakes. Typically, 10 g of freeze-dried sediments were extracted for analysis, but the sediments from lakes directly treated with toxaphene contained sufficient amounts of these compounds that could be measured in samples as small as 1.5 g dry weight.

Sediments from both lakes were dated using ^{210}Pb analysis (Eakins and Morrison 1978) and varve counts (varves are annual sets of laminae) in Chatwin Lake only. Maximum toxaphene concentrations further confirmed the approximate depth representing the year of treatment.

Rainbow Trout Samples

Stocked rainbow trout (~2 yr old) were collected from the two treated lakes (Peanut and Chatwin) using 7.6 cm (3-inch) gill nets. Fish were kept in frozen storage until subsampling and analyses. Thirty to forty grams of skinned dorsal muscle from three fish from each lake were removed for toxaphene analyses. Percent of dorsal muscle that was comprised of lipid was calculated following lipid extraction (explained below).

Stable nitrogen isotope ($\delta^{15}N$) measurements of the same muscle samples were made according to methods described by Hesslein et al. (1993 and 1991). Briefly, tissue was wet digested by nitric acid priciptation of $BaSO_4$. Modified Dumas combustion in sealed tubes was used to produce N_2, with all delta values reported relative to air. A dual-inlet isotope ratio mass spectrometer (VG 602E) was used for analyses, with precision for $\delta^{15}N$ of 0.3‰.

Toxaphene (CHB) extraction and GC analyses

The procedures for extraction of CHBs were described by Muir et al. (1990; 1994). Briefly, fish tissue was homogenized by grinding samples with dry ice, and lipid was removed by automated gel permeation chromatography. Freeze-dried sediments were Soxhlet-extracted with dichloromethane (DCM) for 16 h; prepared fish tissues were Soxhlet-extracted with 1:1 hexane:DCM. Internal standards of aldrin and octachloronaphthalene (OCN) were added at the extraction step. Sulfur was removed using activated Cu filings. CHBs in sediment and fish extracts were separated from PCBs by chromatography on Florisil (Muir et al. 1990).

Extracts were analysed by capillary gas chromatography with electron-capture detection (GC-ECD), using a Varian 6000 GC as described by Muir et al. (1990; 1994). Samples were injected (splitless mode) on a 60 m x 0.25 mm i.d. DB-5 column (film thickness 0.25 µm) with an initial temperature of 100°C then programmed at 15°C.min^{-1} to 150°C and 3°C.min^{-1} to 265°C. Carrier gas was H_2 (about 1 mL.min^{-1}) and make-up gas was N_2 (40 mL.min^{-1}). Toxaphene was quantified using a procedure similar to that described by Ribick (1982). Twenty peaks in the analytical standard (toxaphene mixture obtained from the US EPA, Cincinnatti OH) were selected based on their prominence in the toxaphene standard and a single response factor (SRF) was determined based on peak area. Toxaphene concentration was calculated by multiplying the area of peaks with the same retention times in the sample chromatogram by the SRF. Toxaphene concentrations in fish muscle are reported as both ng.g^{-1} wet weight and ng.g^{-1} lipid.

Confirmation by GC-ECNIMS

The presence of CHBs in Chatwin Lake sediments was confirmed by GC-ECNIMS in selected ion mode, using a Kratos Concept high resolution mass spectrometer and a Hewlett-Packard Model 5890 GC equipped with a 60 m x 0.25 mm i.d. DB-5 MS column (He carrier gas). Two ions from the M^- (m/z 342.8962 + 343.9041) and $(M\text{-}Cl)^-$ (m/z 308.9352 + 310.9323) cluster for Cl_6 bornanes and two from the $(M\text{-}Cl)^-$ cluster for the Cl_7 (m/z 342.8962, 344.8933), Cl_8 (m/z 376.8573,

378.8543) and Cl_9 (m/z 410.8183, 412.8154) components were monitored at 10,000 resolution. Methane was used as the moderating gas and the ion source temperature was 120°C. The electron energy was 200 eV and the ion acceleration voltage was 5.3 kV. Perfluorokerosene (PFK) was used as the mass calibrant.

Results

Sediment Toxaphene Profiles

Maximum total toxaphene concentrations in the sediments from both treated lakes were found at depths representing the years in which toxaphene treatment occurred (1961-1962, Fig. IV-1a, b). The appearance of toxaphene maxima agreed with ^{210}Pb dates for Peanut Lake, and ^{210}Pb combined with varve counting estimates for Chatwin Lake (Miskimmin and Schindler 1994). These maxima were 500 $ng.g^{-1}$ (dry weight) for mesotrophic Peanut Lake and 1600 $ng.g^{-1}$ for eutrophic Chatwin Lake (Fig. IV-1). Surface sediments in the treated lakes contained 53 and 112 $ng.g^{-1}$ toxaphene for Chatwin and Peanut Lakes, respectively, whereas concentrations in the untreated lake sediments were undetectable (<0.1 $ng.g^{-1}$).

CHB Patterns in GC-ECD and GC ECNIMS Chromatograms

The patterns of CHB peaks for Peanut Lake sediments at 20-22 cm were similar to the toxaphene standard (Fig. IV-2 a,b). Chatwin Lake sediments at 11-12 cm showed the same pattern (not shown). The early part of the chromatograms showed only a slight enhancement of the hexa- and heptachlorobornane area. Thus, the original toxaphene remaining at these depths (representing 1961 or 1962) was essentially unchanged after 32 years in anaerobic sediments.

In more recent sediments, Chatwin Lake samples (eg. 9-10 cm) had GC-ECD peak patterns similar to the Peanut Lake sediments (9-11 cm) of about the same age (~1970; Fig. IV-2 c,d), but were very different from technical toxaphene and from the 1962 sediments discussed above. The pattern was characterized by the absence of the octa- and nonachlorobornanes and the presence of a prominent peak (labelled "T-sed", retention time ~31 min) along with other unidentified and early eluting, less chlorinated compounds. The other, previously identified toxaphene peaks are indicated on the chromatogram (T1 through CB9), although these later eluting compounds were not found in these lakes (Fig. 2-IV).

GC-ECNIMS confirmed the presence of the dominant heptachlorobornane (Cl_7; m/z 344.8933) in recent sediments from Chatwin Lake. This component was only a minor peak in technical toxaphene but was a dominant peak in sediments deposited in the 1970's and 1980's representing >90% of total peak area of the Cl_6 (m/z 343.9041) and Cl_7 (m/z 344.8933) ions monitored by GC-ECNIMS (Fig. IV-3 a,b). Also present were hexachlorobornanes (m/z 343.9041, Fig. IV-3 c) which are not present in the toxaphene standard (Fig. IV-3d). The $(M\text{-}Cl)^-$ ions of the hexachlorobornanes gave better sensitivity than the M^- ions (data not shown). Several of the unidentified peaks eluting prior to "T-sed" in Fig. IV-2 can be tentatively identified as hexachlorobornanes based on their matching relative retention times in GC-ECNIMS and GC-ECD chromatograms. GC-ECNIMS chromatograms of samples from the

depth representing the year of treatment of Chatwin Lake (11.5 cm), had the pattern of hepta-, octa- and nonachlorobornanes closely resembling technical toxaphene, similar to the findings with GC-ECD (not shown).

Toxaphene in Stocked Rainbow Trout

Toxaphene concentrations in 2-yr-old rainbow trout muscle from Chatwin Lake averaged 68.3 ± 22.5 $ng.g^{-1}$, and for Peanut Lake 11.7 ± 6.3 $ng.g^{-1}$. Percent lipid was also higher in fish from Chatwin than Peanut Lake (Table IV-1). GC-ECD peak patterns in fish tissue extracts (not shown) had similar patterns as those for recent sediments (Fig. IV-2 c,d) with a prominent "T-sed" peak. GC-ECNIMS confirmed the dominance of the heptachlorobornane ("T-sed") and hexachlorobornanes in rainbow trout from Chatwin Lake (Fig. IV-4 a-d). The GC-ECNIMS peak pattern in fish differed slightly from that in sediments. Heptachlorobornanes eluting prior to "T-sed" (at retention times of 20-23 min) were not as prominent as in sediment while early eluting hexachlorobornanes (18-19 min) were not detected. The three hexachlorobornane peaks at 21 to 22 min (Fig. IV-4c) in the fish extracts had identical relative retention times to those in sediments.

Discussion

Concentrations of toxaphene in the surface sediments of the treated lakes were much higher than sediments of the untreated lake, showing that some of the applied toxaphene has persisted for over 3 decades. Because toxaphene was undetectable in sediments from the untreated lake, atmospheric sources of toxaphene in these treated lakes are negligible compared to the *in situ* source, unlike in other toxaphene-contaminated systems (e.g. Kidd et al. 1993). It is also possible that any atmospheric toxaphene is more diluted or degraded in this productive untreated lake compared to other remote locations. Recent sediment residues no longer resemble technical toxaphene, but consistently exhibit an unique CHB "fingerprint" similar to that found in fish from these lakes (Figs. IV-3, IV-4). Others have found a reduced number of congeners in biota, indicating similar extensive alteration of the original mixture (Bidleman et al. 1993; Stern et al. 1992) although the altered toxaphene did not have the dominant peaks observed in samples from these treated lakes.

This is the first time that a heptachlorobornane has been detected as the majority of a toxaphene residue in either sediments or fish tissue. Heptachlorobornanes are prominent in water and air samples (Bidleman et al. 1989; Barrie et al. 1993) but their actual structures have not been identified. I was unable to further characterize "T-sed" by mass spectrometry because of the limited sample size from each sediment slice. The prominence of "T-sed" in fish as well as sediments suggests that sediments are the source of "T-Sed" to the fish. Further, "T-Sed" may be structurally similar to other persistent CHBs. Recalcitrant CHBs in fish and marine mammals are characterized by a single Cl^- at the 2, 3, 5 and 6 positions on the 6-membered ring, two chlorines at the 8 position, and two at the 10 position (Hainzl et al. 1993). However, lake sediments (Muir et al. 1994), water, air and biota (Bidleman et al. 1989; Bidleman et al. 1993) do not show such a prominent CHB peak eluting

earlier than the bulk of the components in the toxaphene standard.

Surprisingly, some of the original toxaphene was essentially undegraded as evidenced by the resemblance to technical toxaphene of the compound from buried sediments dated to the early 1960's (Fig. IV-2a) and the high concentrations at those depths. However, the extensively altered nature of the compound found in sediments above and below the 1962 horizon was not unexpected given the known pathways of degradation. Reductive dechlorination is the most likely pathway responsible for the presence of the hexa- and heptachlorobornanes. Under anoxic conditions, toxaphene degradation has been found to occur both microbially (Saleh and Casida 1978; Mirsatari et al. 1987) and chemically (Williams and Bidleman 1978). With a lower chlorine content relative to most toxaphene components, the hexa- and heptachloro-congeners are expected to be more water soluble and to have lower sediment adsorption coefficients than the parent compound. Hence, the lower chlorinated CHBs became separated from the stable, more particle-bound parent material.

Given the lack of physical mixing of the deepwater sediments in these lakes, porewater diffusion is the most likely explanation for the broad distribution of CHBs. For comparison purposes, the diffusion coefficient (D_e) in water at 10°C for $C_{10}H_{11}Cl_7$ and $C_{10}H_9Cl_9$ CHBs are 1.26×10^2 $cm^2.y^{-1}$ and 1.17×10^2 $cm^2.y^{-1}$, respectively, using the Hayduk and Laudie method (Lyman et al. 1982).

Effective diffusivities (D_{eff}) in sediment porewaters are a function of the sediment sorption coefficient (K_d, concentration in sediments ÷ concentration in water), porosity and bulk density (Eisenreich et al. 1989). K_d values for hepta- to nonachlorobornanes could not be measured in this study because of lack of porewater data. However, in Lake Ontario sediments K_d values for mirex (HCB), which is similar in molecular weight and chlorine content to these hepta- to nonachlorobornanes, ranges from 1800 to 4700 (Eisenreich et al. 1989). Utilizing these values for Cl_7 and Cl_9 CHBs, gives D_{eff} values of 5.7×10^{-2} and 2.0×10^{-2} $cm^2.y^{-1}$ respectively, much like those for PCBs (Eisenreich et al. 1989). Penetration depth (z) can be calculated from the equation (Edgington et al. 1991):

$$z = (4 \times D_{eff} \times t)^{1/2}$$

where t = time (=30 yr). Diffusive penetration in Chatwin Lake sediments could therefore range from 1.6 cm for nonachlorobornanes to 2.7 cm for heptachlorobornane congeners. This might account for the relatively broad peak of unaltered toxaphene observed between 10 and 13.5 cm depth in the Chatwin Lake core (Fig. IV-1) and may explain in part the predominance of the heptachlorobornane in slices above and below the toxaphene horizon.

I am not sure why downward diffusion appears to have occurred in Chatwin Lake but not in Peanut Lake sediments. It is possible that a 1 cm-thick silt/clay band at 24 cm in Peanut Lake sediments prevented significant downward transport. Veith and Lee (1971) found that particle-bound toxaphene was transported downward in the sediments of two Wisconsin lakes mainly because of physical mixing rather than molecular diffusion. Except for the slump that occurred in the mid-1960's in Peanut Lake, neither physical mixing nor bioturbation of profundal sediments occurs in these lakes, as evidenced by laminations in the cores.

Another possibility for the presence of altered toxaphene in sediments above the 1962 horizon is contaminant focusing from shallow to deep sediments. The process by which more sediments accumulate at deeper sites than shallow ones was first described as "sediment focusing" by Likens and Davis (1975). If I assume that toxaphene was applied evenly over the surface of the lakes, it is likely that a portion of it became associated with near-shore sediments, and gradually focused to deeper sediments by means of turbulence and gravity. In this way, "T-sed" levels did not drop to zero in more recent sediments, but rather were replenished by the littoral sediment supply, much as has been shown to occur in small lakes with radionuclides like ^{137}Cs and ^{210}Pb (Anderson et al. 1987). Toxaphene analysis of near-shore sediments that are exposed to mixing would indicate whether "T-Sed" in deep sediments is continually "supported" from this location.

The highly altered peak pattern in the sediments and fish from the toxaphene-treated lakes illustrates the difficulty in quantifying toxaphene. Although the standard use of a SRF is probably accurate where the pattern of CHB peaks resembles technical toxaphene, as in Peanut Lake slice 20-22 cm and Chatwin slice 11-12 cm, it becomes problematic where the chromatogram consists of only one or two major peaks. I based my quantification on a SRF by GC-ECD and ECNIMS in order to be compatible with most of the published literature on toxaphene. Where the technical toxaphene pattern is absent as in all other samples, a method such as a representative chlorobornane mixture as formulated by Lach and Parlar (1990), or using individual response factors may be more appropriate.

No inferences may currently be made about the toxicological properties of the individual compound "T-sed", found here. However, some environmental residues of toxaphene can be at least as toxic as the parent compound to fish (Isensee et al. 1979; Harder et al. 1983) and insect larvae (Matsumura and Gooch 1988), and have nearly the same relative amounts of toxic components as the technical material (Gooch and Matsumura 1985).

The higher lipid content of Chatwin Lake fish may account for the higher CHB concentration in fish despite lower concentrations in surface sediments. Organochlorine accumulation is often related to length of time of exposure, food chain length and/or to the lipid content of fish (Rasmussen et al. 1990). An important factor to note is the relatively short period of time that these stocked fish were in the lakes. The fish in these treated lakes were about 2 years old, having been stocked the previous year. If other fish stocked at the same time continue to accumulate CHBs at these rates, particularly in Chatwin Lake, it is possible that CHB levels could increase as fish grow older.

Alternatively, the fish from Chatwin Lake may have had higher toxaphene (T-Sed) concentrations because they were feeding at a higher trophic level. Nitrogen isotopes have been used as food chain tracers. In general, organisms with high $\delta^{15}N$ occupy higher trophic levels (Peterson and Fry 1987), and contain higher concentrations of contaminants. For Peanut Lake, tissue from trout measured 8.25 ± 0.08‰, and for Chatwin, trout measured 12.27 ± 0.20‰ (Table IV-1). The difference between them of 4‰ would indicate that the trout in Chatwin Lake are feeding at a

higher trophic level because each level is reflected by an increase in $\delta^{15}N$ of 3 to 5‰ (Peterson and Fry 1987). This information would not have been apparent from stomach content analyses alone, because fish from both lakes contained similar invertebrate prey items. Unlike $\delta^{15}N$ measurements, single measures of stomach contents are poor indicators of year-round trophic position because of the lag time between ingestion of food items and assimilation to tissue (Hesslein et al. 1993). Further studies, including stable isotope measurements of invertebrates in the lakes, are necessary to evaluate the food chain hypothesis.

The absence of some early eluting hexa- and heptachlorobornanes in fish extracts (compared to sediments) suggests that the rainbow trout have some capability to degrade or excrete CHBs. Delorme et al. (1993) found that an octachlorobornane (T2) had a significantly shorter half-life (294 d) than a nonachlorobornane (T12; 376 d) following interperitoneal (abdominal cavity) injection of adult lake trout of similar in size to the rainbow trout sampled in this study. As a lower chlorinated form, the half-life of "T-sed" in fish may therefore be in the range of 200-250 d ($0.003.d^{-1}$). The fish in these treated lakes are subjected to a continual source of chlorobornanes originating in sediments, so the rates of degradation/excretion relative to accumulation will determine the body burden of chlorobornanes over the life of the fish.

The slow elimination of "T-sed" could give rise to significant bioaccumulation in older fish, although rapid growth of young stocked fish ($0.003\text{-}0.004.d^{-1}$) might dilute tissue concentrations. I estimated the bioavailability of CHBs by calculating biota-sediment accumulation factors (BSAF; Parkerton et al. 1993) for rainbow trout in the two lakes (Table IV-1). Average BSAFs of 1 for Peanut Lake fish and 4 for Chatwin Lake are lower than BSAFs generally found for toxaphene in salmonids. For example, BSAFs in the range of 30-50 were found for toxaphene in insectivorous lake trout from small Precambrian Shield lakes (NW Ontario) that receive only atmospheric inputs of CHBs (D.C.G. Muir, unpublished data). Chlorinated pesticides such as chlordane and DDT have been observed to have BSAFs >10 in fish depending on trophic level and the magnitude of the sediment/water partition coefficient (K_d, Parkerton et al. 1993). Therefore the toxaphene (mainly "T-sed") levels in 2-yr-old fish in Chatwin and Peanut Lakes are probably well below steady-state concentrations that could be achieved after prolonged exposure. Given these examples, other lakes that were directly treated with toxaphene and that have active fisheries, should be re-examined. Previously unrecognized forms of toxaphene may be present at elevated levels in biota from these lakes, even decades after treatment.

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Table IV-1. Total weight, toxaphene concentration (wet and lipid weight basis), percent lipid and $\delta^{15}N$ in muscle of 2-year-old Rainbow Trout collected in 1993 from Chatwin and Peanut Lakes. Both lakes were treated with toxaphene in 1961 or 1962. Toxaphene quantified in dorsal muscle by GC-ECD using SRF. CHB peaks were confirmed with GC-ECNIMS.

	Fish Weight (g)	% Lipid	$\delta^{15}N$(‰)[a]	Toxaphene ($ng.g^{-1}$) wet wt	Lipid	BSAF[b]
Chatwin Lake						
Fish #1	644	7.60	12.0	100	1320	4.6
Fish #2	511	4.89	12.5	50	1020	3.6
Fish #3	587	6.97	12.2	55	790	2.8
Peanut Lake						
Fish #1	482	1.36	8.2	18	1320	1.9
Fish #2	479	2.38	8.3	14	590	0.8
Fish #3	443	1.35	8.2	3	220	0.3

a- $\delta^{15}N$ is a stable isotope used as a trophic indicator. Higher $\delta^{15}N$ indicates feeding at a higher trophic position, especially if the difference is 3.4 or greater.

b- Biota-Sediment Accumulation Factor = lipid based [Tox] ÷ sediment organic carbon based [Tox]; OC = 18.5% of sediments (dry wt) in Chatwin Lake and 15.9% in Peanut Lake assuming OC as = 0.4 of %LOI.

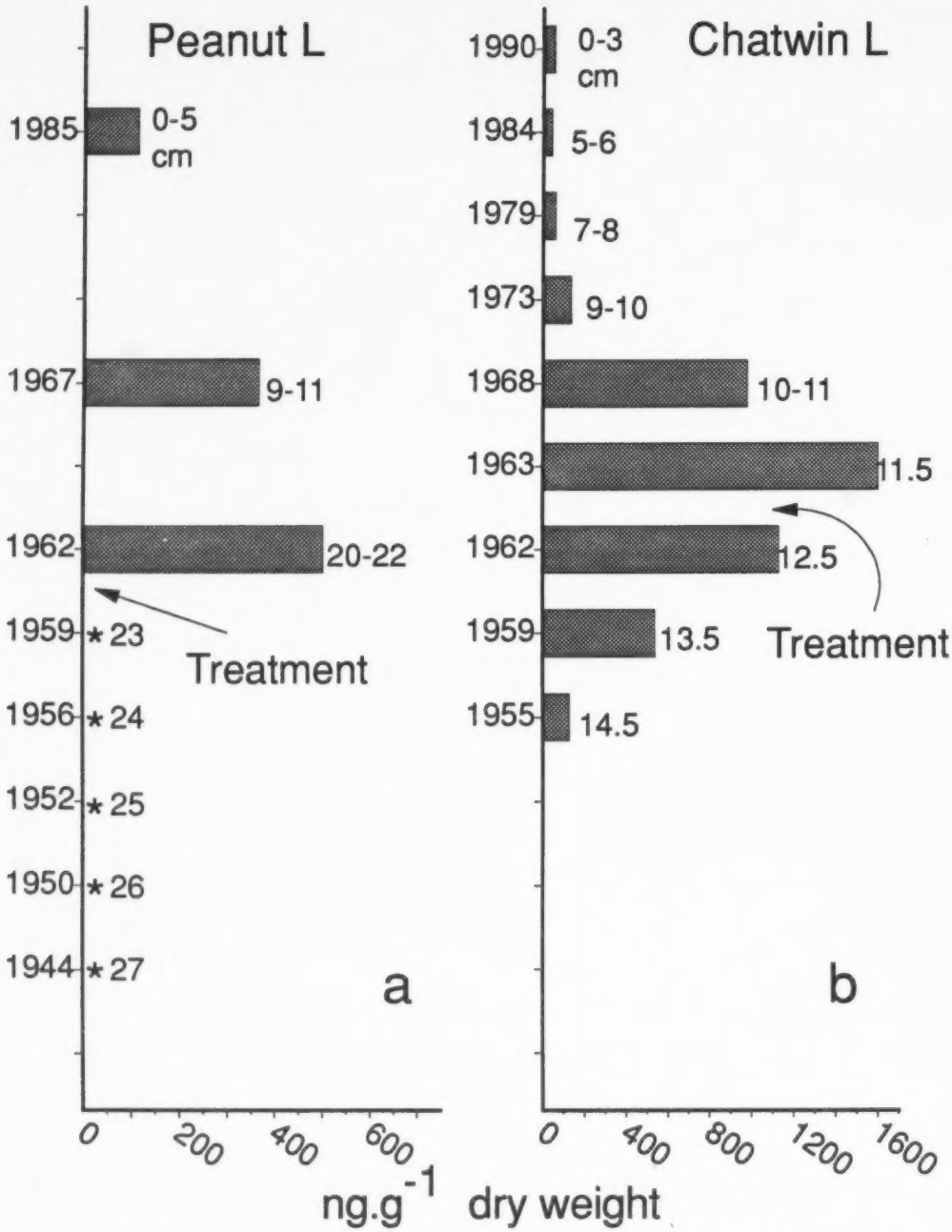

Figure IV-1: Toxaphene concentration profiles by depth and age in slices of freeze cored sediments in (a) Peanut Lake and (b) Chatwin Lake, Alberta. Bars are shown for all sample depths analysed. Note that toxaphene was non-detectable (*) in samples from Peanut Lake below 22 cm. Both lakes were treated with toxaphene in the early 1960's.

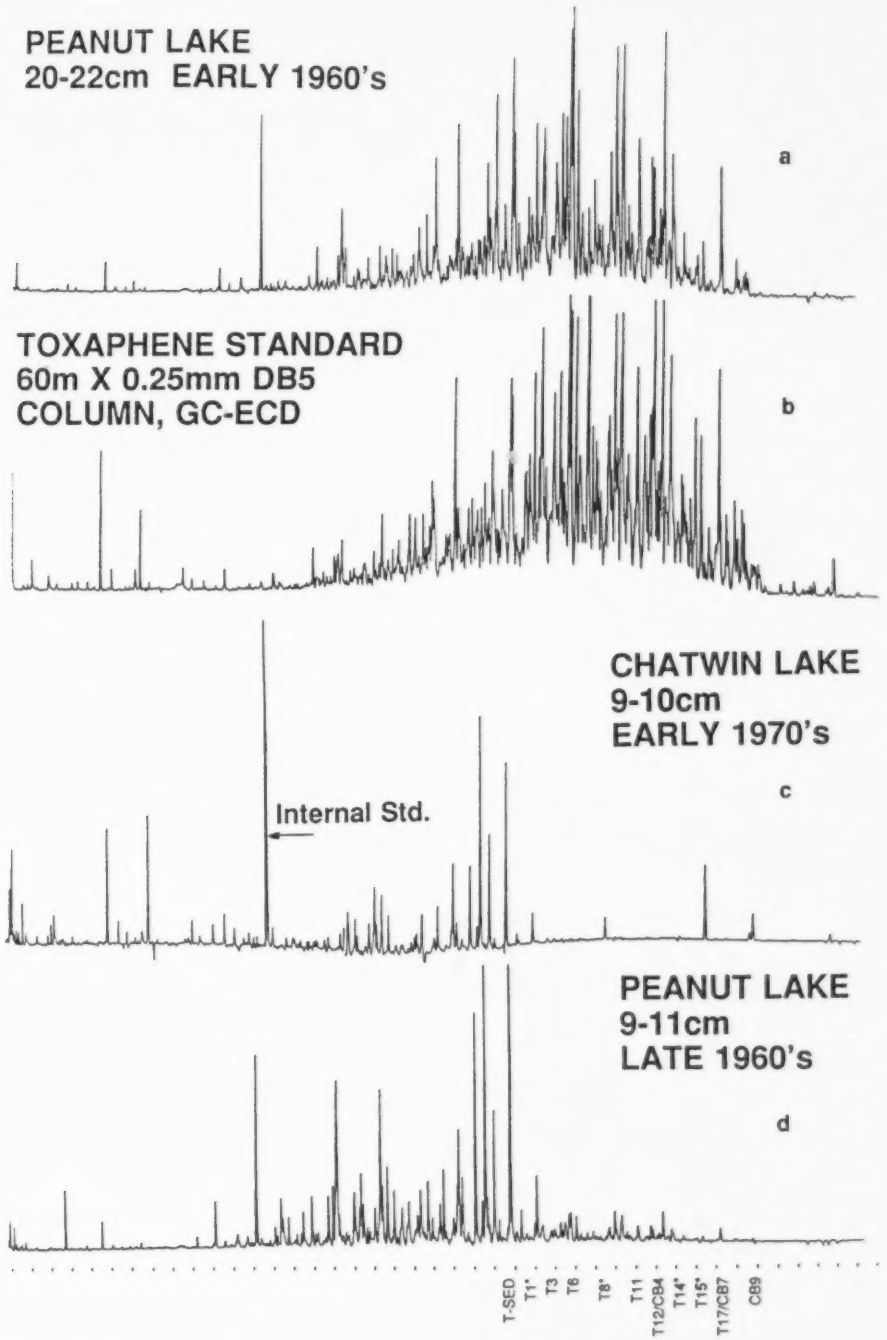

Figure IV-2: GC-ECD chromatograms of chlorobornanes in lake sediments. **a**- Peanut Lake at 20-22cm depth in sediment (1961); **b**- toxaphene standard; **c**- Chatwin lake at 9-10 cm (1972); **d**- Peanut Lake at 9-11 cm (1969).

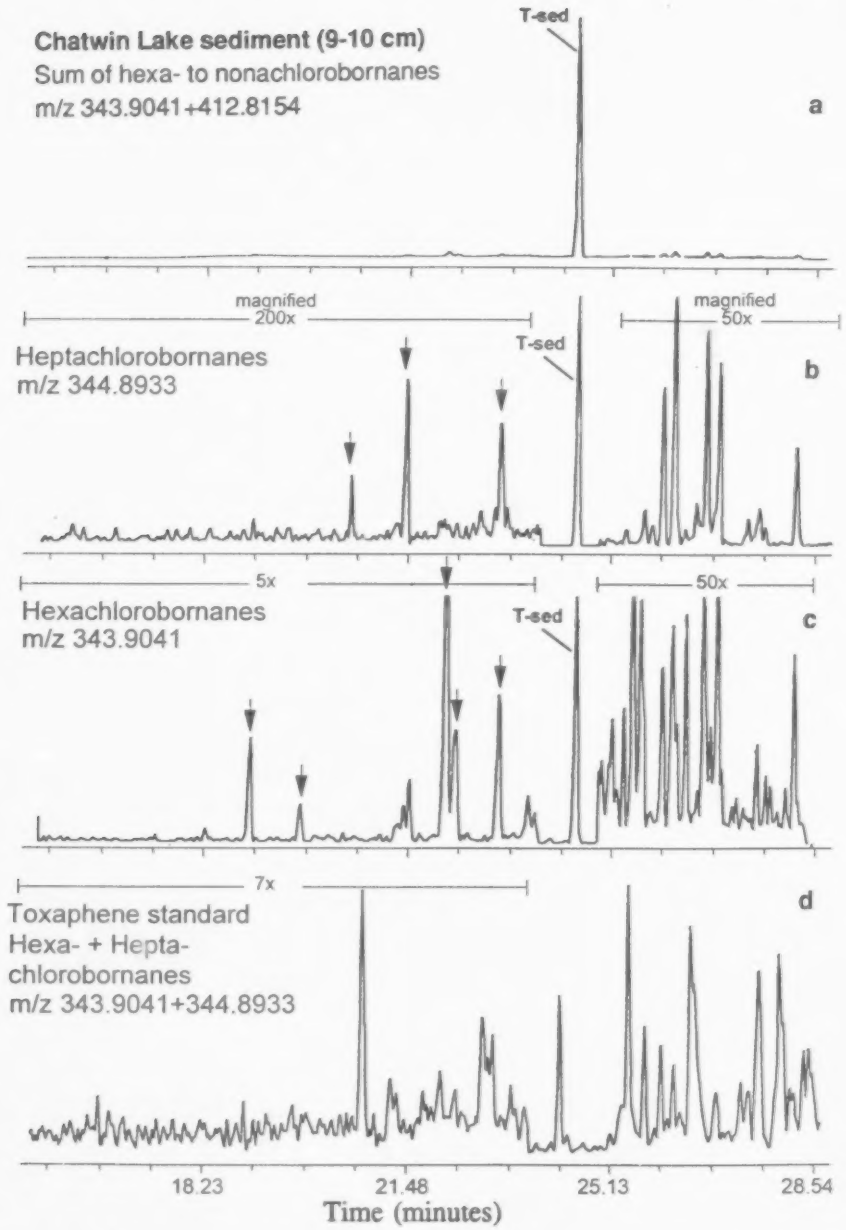

Figure IV-3: GC-ECNIMS selected ion chromatograms for hexa- and hepta-chlorobornanes in sediment extracts (a,b,c) and in the toxaphene standard (d). Areas to the left and right of "T-sed" are magnified as indicated to enhance the resolution of minor peaks. Arrows indicate the peaks not present in the toxaphene standard.

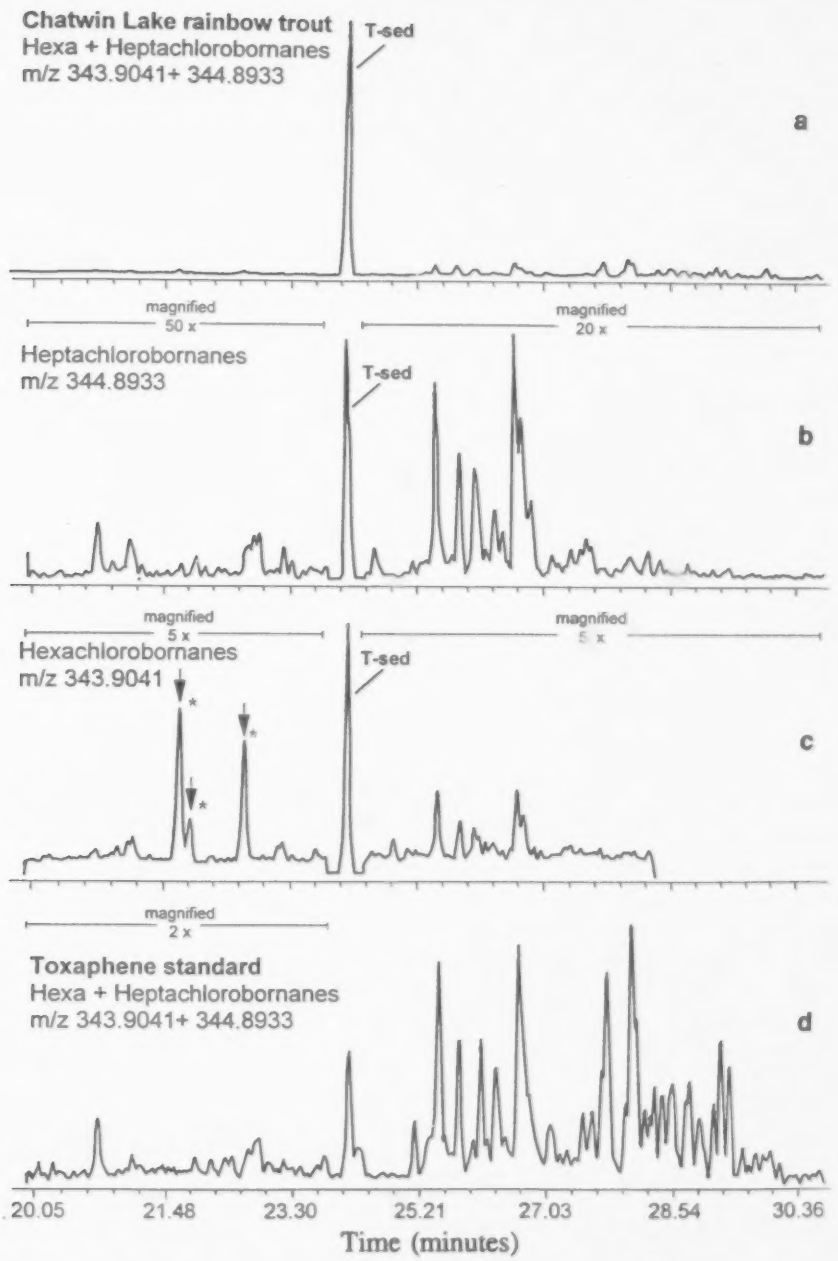

Figure IV-4: GC-ECNIMS selected ion chromatograms for hexa- and hepta-chlorobornanes in Chatwin Lake rainbow trout tissue (a,b,c) and in the toxaphene standard (d). Areas to the left and right of "T-sed" are magnified to enhance the resolution of minor peaks. Arrows and * indicate the peaks not present in the toxaphene standard, but are the same as in sediments.

V. GENERAL DISCUSSION

The practice of treating lakes with toxaphene was abandoned many years ago, but my results indicate that there were inadvertent short- and long-term consequences to lake biota. Invertebrate communities and algal assemblages in some lakes were significantly changed with treatment (Chapters II and III). All lakes showed long-term increases in large-bodied invertebrates that were either directly caused by toxaphene or by subsequent changes in food webs.

Surface sediments and young fish contain degraded toxaphene 30 years after the treatments (Chapter IV). Sport fish in these treated lakes are not as seriously contaminated as in other areas (e.g., Winger 1989; Kidd et al. 1993). However, as discussed in Chapter IV, the exposure period was relatively short for these 2-yr old fish, and concentrations will increase with time as the fish gain weight. The bioaccumulation of toxaphene residues by all contemporary organisms is a continuing legacy in toxaphene-treated lakes. Although toxaphene is no longer used, future lake poisonings with rotenone are planned in Alberta. Trout stocking is an ongoing practice with the Department of Fish and Wildlife. My results may help others to appreciate that such "lake rehabilitations" cause more than short-term effects to non-target organisms.

The direct effects of toxaphene application to non-target organisms ranged from extreme for some (e.g. *Bosmina* in Chatwin; algal assemblages in Annette) to undetectable for others. The latter were apparently either resistant to the poison, in reduced contact with the poison by use of localized refugia, or recovered more quickly than my methods could discern (i.e. < ~1-2 years; see Chapters II and III). This would include Chironomidae in all lakes, many of the Chydoridae in two lakes (Annette, Chatwin), and algal assemblages in the most eutrophic lake (Chatwin). As discussed in Chapter II, chironomids may have proven more sensitive had more detailed taxonomic identifications been possible.

It is not surprising that invertebrates from Chatwin Lake were affected most strongly because this lake received a concentration about three times that used in Peanut Lake. Lakes in Alberta with higher alkalinities were regularly treated with higher toxaphene concentrations. The alkalinities of Chatwin, Peanut and Annette Lakes are approximately 16, 6, and 2.5 meq.L^{-1}, respectively. While I was not able to ascertain the toxaphene concentration used in Annette Lake, an alkalinity-based estimation makes it likely that the amount was lower than that used in Peanut Lake.

The responses of organisms in Peanut Lake and Annette Lake were similar to the response of zooplankton to rotenone found by Anderson (1970), where most species recovered by the following year. As in the toxaphene-treated lakes, chaoborids and large-bodied cladocerans reached high abundances in the years following rotenone treatment. Only in Chatwin Lake was *Bosmina* strongly affected and ultimately failed to recover in the presence of abundant invertebrate predators (see Chapter II). The slowest recovery recorded by Anderson (2.5 years) was a copepod that had not reached reproductive maturity at the time of rotenone treatment. Unfortunately, copepods are among the organisms that do not preserve in sediments, so the only way to study effects on them is through long-term monitoring.

Reduced planktivory following salmonid introductions appeared to be responsible for observed longer-lasting effects on invertebrates (Carpenter et al. 1987; Elser et al. 1987). This food web response was consistent among all three lakes despite some overlap in the diet of trout and the extirpated fish species in these lakes (mainly perch, walleye, cyprinids; Nelson and Paetz 1992). While the diets may be qualitatively similar, the lower abundance, choice of habitat within the lakes, and other relative differences in the characteristics of trout would account for the switch in invertebrate dominance to large-bodied taxa following trout stocking.

The long-term changes to the lake communities caused by trout stocking are similar to those lakes that have been successfully stocked with hatchery trout, whether or not the lakes were poisoned (e.g., Lamontagne and Schindler 1994). In Alberta, the list of lakes that were stocked with trout, with or without rotenone poisoning, is much more extensive than the list of toxaphene-treated lakes (see Appendix C). If regulators are at all concerned about the ecological integrity of the natural ecosystems in their jurisdictions, the practice of stocking of non-native fish should be discontinued.

Perhaps the biggest long-term concern from an ecosystem health viewpoint (including human health) arising from this research is the finding of residual toxaphene in sediments and fish today (Chapter IV). The treated lakes discussed in this thesis, as well as several others in Alberta, are currently maintained as recreational trout fisheries. Anglers are exposed to toxaphene residues each time they consume their catch. Other organisms at the top of the food chain, like fish-eating birds, might also accumulate potentially harmful concentrations (Winger 1989).

Toxaphene has been assumed to be effectively immobilized after burial in lake sediments, for it is very hydrophobic. In contrast, the heptachlorobornane "T-Sed", that was detected here, may be highly mobile in sediments. It accounted for most of the residual toxaphene, but little is known about its structure, toxicity, bioaccumulation, and behaviour in the environment. Partial dechlorination may reduce the contaminant's affinity for particles, allowing it to diffuse through sediments. It may then be accumulated by fish from the water or through their diet. Decades-old toxaphene is the likely source of T-Sed, because samples from untreated lakes are depleted in T-Sed, although they may contain less degraded toxaphene deposited via long-range atmospheric transport (Stern et al. 1992; Kucklick et al. 1993; Donald and Miskimmin in prep.). The scarcity of T-Sed in lakes where all toxaphene is from atmospheric sources suggests that T-Sed is less volatile than the components typically transported in the air. Thus, T-Sed remains and disproportionately accumulates only at sites where toxaphene was originally used.

Because significantly higher $\delta^{15}N$ values were found in trout from Chatwin Lake compared to Peanut Lake (Table IV-1), I hypothesize that similar invertebrate taxa from these lakes may differ in the trophic level at which they are feeding. If, for example, *Gammarus* are herbivorous in Peanut Lake, and predaceous/omnivorous in Chatwin Lake, $\delta^{15}N$ contents would be expected to be higher in the organisms from Chatwin. Because predators bioconcentrate contaminants to a greater degree than herbivores (Evans et al. 1991), ultimately, fish from lakes containing abundant predaceous invertebrates would have both higher $\delta^{15}N$ and toxaphene concentrations.

Toxaphene remains an important global pollutant because it is still used in third world countries, and is found in areas remote from current utilization sites including the Canadian Rocky Mountains (Donald et al. 1993), the Arctic (Stern et al. 1992), and the Great Lakes (Saleh 1991). In remote areas, high levels of toxaphene are often found in older fish from lakes with exceptionally long food chains (Kidd et al. 1993), similar to PCBs (Rasmussen et al. 1990). Lakes where toxaphene was deliberately added are of special concern because while they may lack extremely old fish and may have short food chains, residual toxaphene is obviously abundant and available. It is clear from my findings and those of Donald and Miskimmin (in prep.) that any lakes that were historically treated with toxaphene are potential sources, rather than sinks, of toxaphene degradation products.

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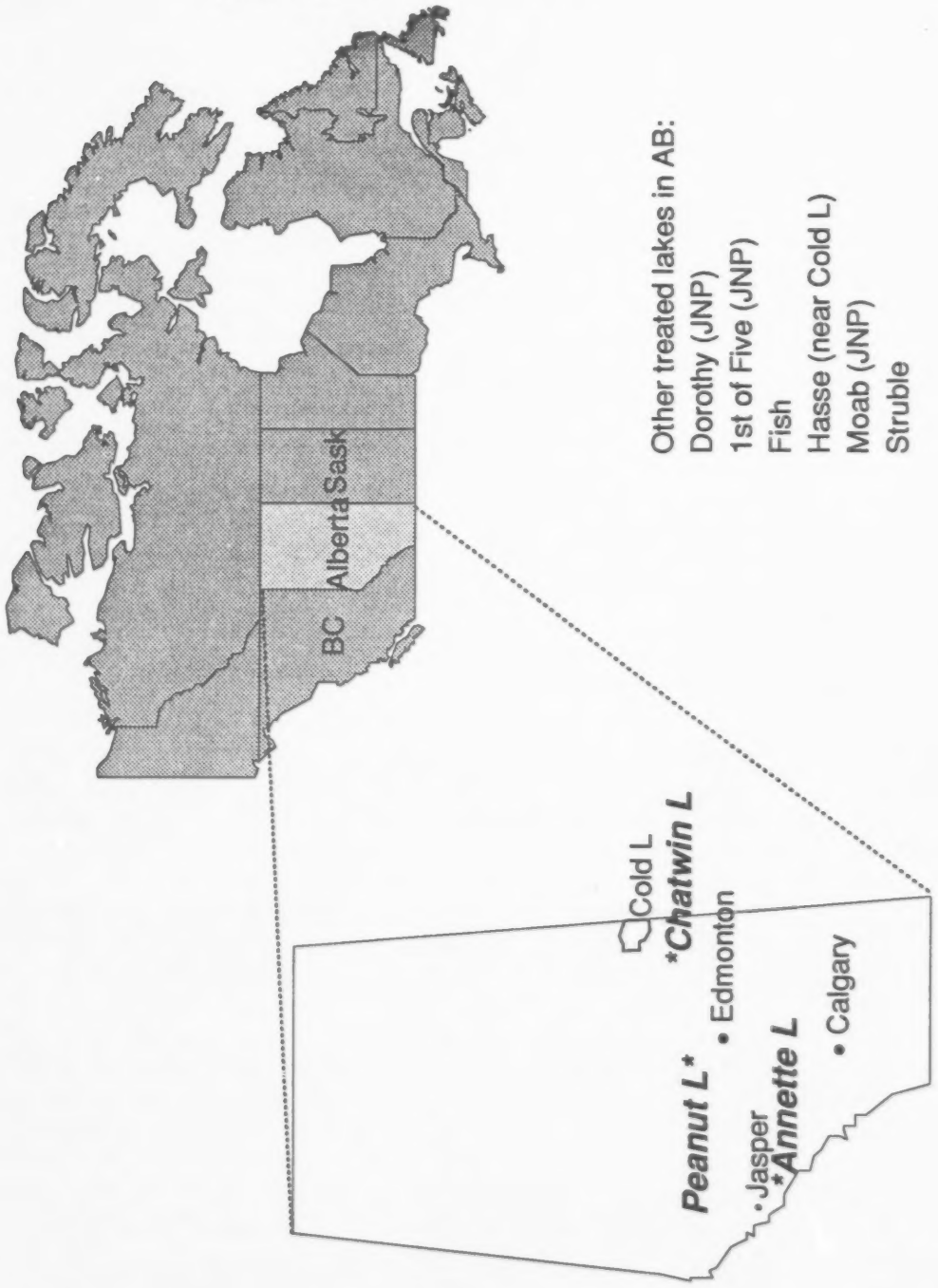
APPENDIX A: Map of Canada and Alberta indicating locations of 3 study lakes. These and other toxaphene-treated lakes listed are shown on detailed southern Alberta Map in Figure I-1. JNP = Jasper National Park.



APPENDIX B: Detailed methodology

Methods described include
1. Freeze-core collection
2. Preparation of cores for subsampling
3. Subsampling
4. Pigment extraction

1. Freeze-core collection

Materials

hollow Al freeze corer
lead weights if needed
rope
8 X 1/2" 1/4-20 hex head bolts
nut driver to fit bolt head
2 X 50 lb blocks of dry ice
2 large coolers
1-2 L methyl hydrate
metal bucket
large funnel
plastic bucket
foil, plastic, & burlap wrapping material
hockey or friction tape
heavy duty insulated gloves
wide paint scraper
hacksaw
safety glasses (important)
tool kit

Cores may be collected in summer from a boat or, preferably, in winter through the ice. The deepest site in the lake is the preferred location if intact chronology is necessary. In summer, calm weather is worth waiting for. At the site, crush a few kg of dry ice in the metal bucket using a hammer, then mix with enough methyl hydrate to make a slurry (wear eye protection). Pour this solution carefully into the corer through the large funnel. Use a screw driver to speed funnelling. Fill the corer to about 10 cm from the top. Bolt the core cap back in place. Depth at coring site should be measured so that the core can be lowered quickly then slowed a few meters from the sediments. Lower the corer and allow to settle into the sediments. To prevent additional settling or tipping during the freezing process, tie off the rope to a float (summer) or a stick across the hole in the ice. Obviously, the ice surface is more stable than a float. Allow the corer to sit for 11-12 minutes. Bubbles will be produced continuously as CO_2 is released due to dry ice sublimation. Retrieve the corer quickly to the surface. Have ready a bucket of water and the wide paint scraper. Hold the corer upright in a tub and

remove excess mud from the core surface by repeatedly turning the core, scraping lengthwise, and cleaning the scraper. Wrap core immediately in stretch wrap and and secure with hockey tape. Use a hacksaw to score the circumference about 10 cm above the sediment water interface, then obliquely tap with a hammer or screwdriver handle to remove the unneeded ice. Do the same with the "nose" section. The nose section is more difficult to remove because of the ice thickness and resistance to thawing around the solid cone. Remove cap and pour the slurry and weights into the metal bucket. Pour warmed (winter) or air temperature (summer) water into the corer to encourage thawing of the inner core. Sediment core should then slide off the outside of the corer. Wrap in foil and label, including direction up and down. Wrap in burlap to protect from breakage. During winter, packing with some snow also adds protection. Store in cooler on dry ice for transport. Store in a freezer until ready for further subsampling.

2. Preparation of cores for subsampling

Materials

Bandsaw with new 3/4" blade
Wood plane blade
Al foil

Cylindrical sediment cores are sliced in lengthwise quarters using a full-sized bandsaw. Put the bandsaw in a walk-in freezer until it equilibrates to the freezer temperature. Dress warmly and simply slice the core in half, then slice each section in half again; can slice through the plastic/foil wrapping. Use a wood plane blade to clean the outside surface of the core section. Remove all contaminated or mixed surfaces, and until laminations are clear and undisturbed. Rinse down with distilled water. For toxaphene analyses, the bandsaw was used to slice depths (ie widthwise) from a frozen core. In this case, contaminated surfaces were removed from all sides with a clean, sharp pocket knife. Wrap in Al foil.

3. Subsampling

Core section may be thawed and subsampled by laminae or at regular depths, if using for animal fossils. Entire sections may be freeze-dried in a large freeze dryer (I used a Virtis Freezemobile 6 for 24 h/section), if to be used for algal pigments. Care must be taken not to sample the underside of the core that was next to the Al corer because approximately 2-5 mm from the corer will be disturbed during the coring process. Tape a ruler alongside the core section with "0" aligned with the sediment-water interface. Remove samples to pre-labelled (scintillation) vials.

4. Pigment extraction

Materials:

Analytical balance, 5 mL Oxford pipet, labelling tape, scissors, marker, small scoopla (to mix & pick up seds), 80:15:5 Acetone:MeOH:H_2O, record book, Acropore™ (0.2 µm) filter setup.

Should have labelled vials containing sections from surface of freeze-dried core. Work in reduced light (green/orange filter) as much as possible. Acetone-rinsed glassware, no acids.

Freeze dry samples in vials for another 5 h to get rid of residual moisture; Mix samples thoroughly prior to subsampling. Weigh 5-7 mg into labelled and tared 4 dram vials. Add 5 mL of 80:15:5, and add a N_2 headspace. Make sure all sample submerged. Store in dark fridge ~20-24 h. After extraction, filter through Acropore filters under pressure; filters good for several (~15) samples, use until clogged. Always double rinse with pure Acetone twice between samples. Dry samples in a stream of N_2 in a dark fume hood. Lower Pasteur pipet tips into vial to dimple the surface, adjusting them closer as solvent evaporates. Takes about 2+ h each to dry. When completely dry, seal in a headspace of N_2, and store in freezer until HPLC analysis.

APPENDIX C: Lake stocking and "rehabilitation" projects taken mainly from Annual Reports of the Alberta Dept. of Lands and Forests/Fish & Wildlife. Completeness or accuracy of this list not guaranteed (copied from old record books and files). Rot = rotenone, TOX = toxaphene, JNP = Jasper National Park.

STOCKED ONLY

YEAR	LAKE NAME	OTHER DETAILS
1931	Not named	3 lakes stocked with Trout
1932	Muir	Stocked: Perch
1932	Mary Gregg	Stocked: Rainbow trout
1932	Cold	Stocked Brook trout 1932-1935
1936		END OF RECORDS UNTIL 1941
1945	Cold	Initial decline of Lk Trout/whitefish
1947	Square	Stocked Rainbow trout
1947	Burntstick	Stocked Rainbow trout
1947	Beauvais	Stocked Rainbow trout
1949	Goldeye	Stocked Rainbow trout
1949	Obed	Stocked Rainbow trout
1949	Sylvan	Stocked Rainbow trout
1949	Butcher	Stocked Rainbow trout
1949	Battle	Stocked Lake Trout
1949	Beauvais	Fish stocked not specified
1953		"The interesting activity...planting Rainbow trout..numerous small lks...".
1972		END OF SPECIFIC RECORDS

POISONED AND STOCKED LAKES

YEAR	LAKE NAME	TOXICANT	OTHER DETAILS
1947	Square	Fishtox	Pike/parasite reduction experiment
1957	ANNETTE	TOX	JNP: Removed Longnose suckers, lake chub; stocked Rainbow trout and Brook trout
1958	Beauvais	Rot	Stocked "trout"
1958	Mitchell	UK	Removed pearl dace & trout
1958	Moab	TOX	JNP: Removed Longnose suckers, lake chub
1958	Struble	TOX	Removed pearl dace and darters
1960	Muir	Rot	Removed resident large trout
1961	Fish	TOX	12 ppb Tox; remove Suckers; Add Rainbow trout
1961	Henderson	Rot	Remove 'goldfish', Pike, Perch & others
1961	PEANUT	TOX	7.5 ppb; Remove Walleye, Perch, minnows; stocked Rainbow trout

Cont'd next page...

1962	CHATWIN	TOX	18.2 ppb-Remove Pike, Perch; detox study 1966; Stocked Rainbow trout
1962	Cavan	Rot	Fish stocked not specified
1962	Hasse-NE (near Cold L)	TOX	Removed Pike, Perch, White suckers; Added Rainbow trout, Brook trout-1964.
1962	Lees	Rot	Removed suckers, stocked "Trout"
1962	Mami	Rot	Fish stocked not specified
1962	Shuster	Rot	Removed Pike, stocked Rainbow trout & Brook trout
1963	Fairfax	Rot	Stocked "Trout"
1964	Blue	Rot	Stocked Brook trout
1965	Phyllis	Rot	Removed dace, sticklebacks; Added Kokanee
1966	Cache	Rot	Fish stocked not specified
1966	Chickakoo	Rot	Stocked Kokanee 1967; later Rainbow trout, Brook trout
1966	Graveyard	Rot	Fish stocked not specified
1966	Reesor	Rot	Fish stocked not specified
1966	Twin-RMH	Rot	Removed suckers; Stocked Kokanee 1967
1968	Fairfax	Rot	Fish stocked not specified
1968	Hasse-Edm	Rot	Stocked Rainbow trout 1970
1969	Chrystina	Rot	Stocked Rainbow trout, Brook trout 1970
1969	Gr.Cache	Rot	Stocked Rainbow trout 1970
1969	PierreGr-3	Rot	Stocked Trout 1970
1969	Victor	Rot	Stocked Rainbow trout 1970
1976	Carson	Rot	Stocked Rainbow trout, Walleye; LAST COMPLETE REHABILITATION
1980s	Lees	Rot	Remove illegally-introduced Redside Shiners
1991	Twin (Rocky Mtn Hse)	Rot	Removed suckers, outcompeting Trout

Note: Head office would like to treat ~ 5 lakes with rotenone in future (pers. comm. David Berry, 1992); Edmonton Regional office is less interested in rehabilitation projects, except for introduced 3-spine sticklebacks in Hasse Lake (west of Edmonton; pers. comm. Michael Sullivan, 1994).

APPENDIX D: Letter from Dr. D.G. Frey (1915 - 1992).

INDIANA UNIVERSITY
DEPARTMENT OF BIOLOGY
Jordan Hall 142
Bloomington, Indiana 47405
(812) 855-
FAX: (812) 855-6705

30 Sept. 1991

Brenda Miskimmin
Department of Zoology
University of Alberta
Edmonton, Alberta T6G 2E9, Canada

Dear Brenda:

You are doing just fine in your identifications. I am not. The only paleolimnology of chydorids I have done is on European material, where the problems are fewer than in North America, or at least farther along toward solution. As between Acroperus and Camptocercus for example, the European Camptocercus has a blunt posterior edge to the headshield, whereas Acroperus has a pointed end. What the chief distinctions are between the North American taxa I don't know, and hence you may have to work this out. That is one of the reasons for having intact specimens on hand.

As to the Pleuroxus species, I have recently submitted a paper in which I divide Pleuroxus into four genera, all those taxa related to aduncus being in the genus Tylopleuroxus, and all the species related to laevis in Picripleuroxus. Trigonellus and uncinatus are in the genus Pleuroxus, and truncata in the genus Peracantha. I had supposed that truncata was the only species in the latter genus, but it seems that procurvus also is. This means now that I shall have to look at the North American species to see in which genus each belongs. So, I can't help you much here, either.

Alona is always a difficult genus. One of the common species in your samples is Alona circumfimbriata, which Megard described from Minnesota. The longitudinal striae on the shell and the series of fine denticles along the posterior ventral angle of the shell are diagnostic. There is another larger species in your samples, which may be quadrangularis. However, I did not find any headshields of postabdomens. For Leydigia I saw only the species leydigi, not acanthocercoides.

What I began doing was going over one coverslip from each level in detail and recording everything I found. Then realizing this would take too much time I began looking only at the circles you drew on the covers. My determinations are given on the four attached sheets. Really the only things I found that you hadn't mentioned were claws and mandibles of Daphnia cf. pulex and one caudal spine of Leptodora. The long antennal segments of Chaoborus are quite common.

I have two suggestions. Your preparations are frequently clumped, so that it is difficult to resolve the overlapping remains. What I do before adding the coverslip is to stir up everything, which seems to separate the various remains satisfactorily. The other suggestion is to make strictly qualitative slides by picking our the best remains and mounting them. Most of your remains are fragmented and hence difficult to put species names on until you know quite positively what species are present in the lake. The "good" remains mounted separately will enable you to tell what species are present, and then after this you will be able to put names on the fragments. One other suggestion is that you work with intact specimens as well. Their

morphology, of course, is what you need to identify what is in the sediment. If you can get exuviae from any of your samples, these are even better than the whole specimens.

You will find out (in fact you already have via this letter) that no person will be able to solve all your problems. All he can do is point you in the right direction and hope that you will get good results. The chydorids of North American are too poorly known to give you much encouragement. For example, none of the species of Acroperus or Camptocercus (except oklahomensis) can be named. To separate them out is going to require a big effort by somebody.

So, I feel you have done a good job thus far. How much more you will do will be determined by what your objectives are. You should be able to put species names on just about everything except Acroperus and Camptocercus. These can be handled by giving a brief description of what the taxa are and then designating each of them 1, 2, 3, etc. or a, b, c, etc. if you don't want to tackle the taxonomy yourself. Someday, someone will have to do it.

A few other comments. The Bosmina shells with the "holes" are probably ephippia. You also have ephippia of Camptocercus and perhaps an Alona. What you can see on them is the slough line bordered by small irregular "cells" where the anterior and ventral part of the shell breaks away from the ephippium. Separating the species of Chydorus is difficult. Here is where the qualitative mounting of "good" specimens may be particularly helpful in seeing the detailed course of the ventral setae on the shell. One of the enigmas to me is the complete lack of Alonella species. I would have thought that at least excisa might be present and also nana.

Good luck on your further studies, and feel free to call on me again if you think I might be able to help.

Sincerely,

David G. Frey

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